PB84-151984

Comprehensive Assessment of the Specific Compounds Present in Combustion Processes Volume 3. National Survey of Organic Emissions from Coal Fired Utility Boiler Plants

Midwest Research Inst., Kansas City, MO

Sep 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-151984

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington DC 20460

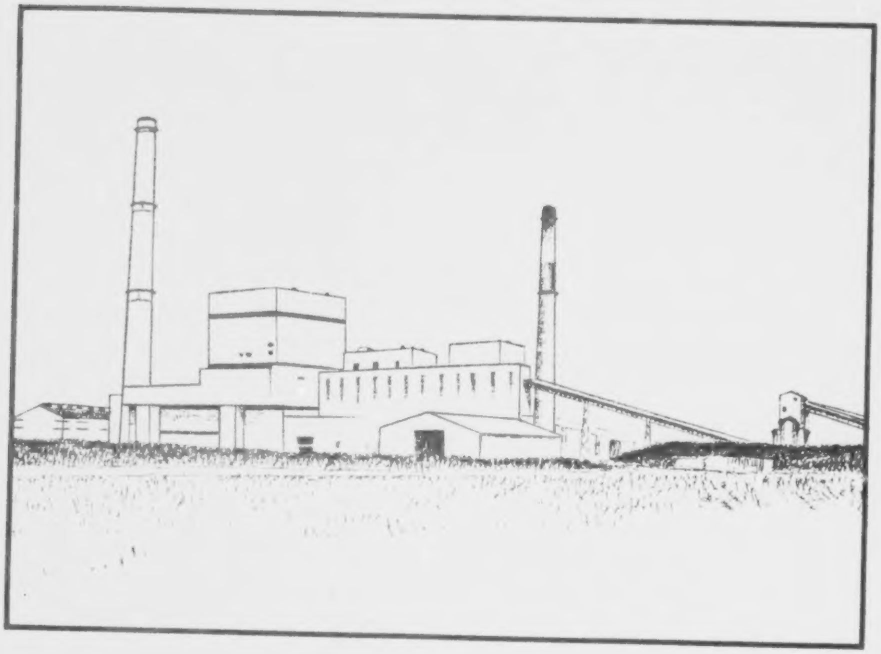
EPA-560/5-83-006
September, 1983

Toxic Substances

EPA

Comprehensive Assessment of the Specific Compounds Present in Combustion Processes

Volume 3
National Survey of Organic Emissions from Coal Fired Utility Boiler Plants



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INFORMATION SERVICE
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SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-560/5-83-006	2.	3. Recipient's Accession No. PB84 151984

4. Title and Subtitle Comprehensive Assessment of the Specific Compounds Present in Combustion Processes. Vol. 3 National Survey of Organic Emissions for Coal Fired Utility Boiler Plants

5. Report Date September 1983

6.

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8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

10. Project/Task/Work Unit No. Task 52

11. Contract/Grant No. 68-01-5915

12. Sponsoring Organization Name and Address

Field Studies Branch
USEPA
401 M Street, SW
Washington, DC 20460

13. Type of Report & Period Covered Final

14.

15. Supplementary Notes

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16. Abstracts

This study was conducted as a part of a nationwide survey to determine organic emissions from major stationary combustion sources. The principal compounds of interest are polynuclear aromatic hydrocarbons (PAHs) and chlorinated aromatic compounds, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). This report describes the methods and results of sampling and analysis activities at the seven plants constituting the nationwide survey of coal fired utility boiler plants.

17. Key Words and Document Analysis. 17a. Descriptors

Combustion, Emissions, Sampling and Analysis

17b. Identifiers/Open-Ended Terms

PAH, PCDD, PCDF

17c. COSATI Field/Group

18. Availability Statement Release to public	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 236
	20. Security Class (This Page UNCLASSIFIED	22. Price

FORM NTIS-35 (10-70)

USCOMM-DC 40329-P71

COMPREHENSIVE ASSESSMENT OF THE SPECIFIC COMPOUNDS PRESENT IN COMBUSTION PROCESSES

VOLUME 3

NATIONAL SURVEY OF ORGANIC EMISSIONS FROM COAL FIRED UTILITY BOILER PLANTS

by

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TASK 52
FINAL REPORT

EPA Contract No. 68-01-5915
MRI Project No. 4901-A(52)

Prepared for

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PREFACE

This draft final report was prepared for the Environmental Protection Agency under EPA Contract No. 68-01-5915, Task 52. The report describes the results of research conducted under Tasks 36 and 52. The tasks were directed by Dr. Clarence L. Haile. This report was prepared by Drs. Clarence L. Haile and John S. Stanley with substantial contributions from Mr. Thomas Walker, Mr. George R. Cobb, and Mr. Bruce A. Boomer.

Technical support was also provided by A. M. Megan, R. V. Northcutt, R. B. Blair, T. Costello, E. Hirsch, M. Valla, B. Mitchell, G. Scheil, M. Hansen, R. Stultz, E. Olson, D. Lacy, M. Gabriel, C. Brown, K. Hall, S. Cummins, T. Arnold, G. Radolovich, J. Onstot, and M. Wickham.

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August 26, 1983

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LIST OF ABBREVIATIONS

acfm	-- Actual cubic feet per minute
dscf	-- Dry standard cubic feet
dscfm	-- Dry standard cubic feet per minute
dscm	-- Dry standard cubic meter
dscmm	-- Dry standard cubic meter per minute
EICP	-- Extracted ion current plots, constructed by computer from scanning gas chromatography/mass spectrometry data
ESP	-- Electrostatic precipitator
HETP	-- Height equivalent to a theoretical plate
HRGC/Hall-FID	-- High resolution (fused silica capillary column) gas chromatography with Hall electrolytic conductivity and flame ionization detectors
HRGC/MS	-- High resolution (fused silica capillary column) gas chromatography with low resolution mass spectrometry detection
HRGC/MS-SIM	-- HRGC/MS operating the spectrometer in a selection ion monitoring mode
HRGC/HRMS-SIM	-- HRGC/MS-SIM with the spectrometer operated at higher than unit resolution (e.g., 10,000 resolution)
PAHs	-- Polynuclear aromatic hydrocarbons
PCBs	-- Polychlorinated biphenyls
PCDDs	-- Polychlorinated dibenzo-p-dioxins
PCDFs	-- Polychlorinated dibenzofurans
PFK	-- Perfluorokerosene
TFE	-- Polytetrafluoroethylene, e.g., Teflon®
THC	-- Total hydrocarbons

SECTION 1

INTRODUCTION

This study was conducted as a part of a nation-wide survey to determine organic emissions from major stationary combustion sources. The principal compounds of interest are polynuclear aromatic hydrocarbons (PAHs) and chlorinated aromatic compounds, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs).

This report describes the methods and results of sampling and analysis activities at the seven plants constituting the nationwide survey of coal-fired utility boiler plants. The statistical design of these studies was constructed by Research Triangle Institute (RTI)[1] based on the results of a two-plant pilot study[2] that was conducted by Midwest Research Institute (MRI) with assistance from TRW, Inc., Southwest Research Institute, and Gulf South Research Institute.

A summary of the results of this study is contained in Section 2 of this report. Section 3 presents recommendations for future work. Brief descriptions of the coal-fired power plants are contained in Section 4. The sampling and analysis methods as applied to these plants are described in Sections 5 and 6. The field test data and analytical results are presented in Sections 7 and 8. Section 9 describes the analytical quality assurance results and the emissions results are summarized in Section 10.

As a part of the sampling and analysis effort, a detailed sampling and analysis methods manual[3] was prepared for use in the current surveys and in similar EPA/Exposure Evaluation Division studies. The methods manual is attached to this report as Appendix A.

SECTION 2

SUMMARY

This study was conducted as a part of a nationwide survey to determine organic emissions from major stationary combustion sources. The principal compounds of interest are polynuclear aromatic hydrocarbons (PAHs) and chlorinated aromatic compounds, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). This report describes the methods and results of sampling and analysis activities at the seven plants constituting the nationwide survey of coal-fired utility boiler plants.

All inputs and outputs (including fuel, water, ash, and flue gas) that were related to the combustion process were sampled during a 5-day period at each plant. Daily flue gas samples (20 m^3) were collected at the outlet of the control devices using a modified Method 5 sampling train. The solid and aqueous grab samples were collected six times per 24-hr period for the test durations. The samples were extracted and analyzed for phthalates, PAHs, PCBs, PCDDs, and PCDFs using fused silica capillary gas chromatography with flame ionization, halide specific, and mass spectrometric detectors.

The polycyclic organic compound emissions from the plant included PAHs and PCBs. These compounds were detected in the flue gases from all four plants studied. Naphthalene was the most abundant PAH compound identified. Emission rates for naphthalene ranged from approximately 500 to 5,000 mg/hr. Polychlorinated biphenyls were determined in flue gases from all seven plants. PCB emission rates ranged from 10 to 8,500 mg/hr. PCBs were also identified in the plant background air from all plants except Plant No. 3. Although the average emission rates for each plant were all higher than the input rates attributable to plant background air, the average input rates were within one standard deviation of the mean emission rates for five of the seven plants. Additionally, the homolog distributions of chlorobiphenyls identified in flue gas and plant background air samples were similar, both between flue gases and background air at the same plant and between plants. The PCBs were comprised primarily of penta- and hexachlorobiphenyls with lesser contributions from tetra- and heptachlorobiphenyls.

The PAHs and PCBs were not identified at significant levels in the solid and aqueous emissions from the seven plants. The levels of extractable organic compounds were low for these samples. Polychlorinated dibenzo-p-dioxins and dibenzofurans were not identified in either the grab samples or flue gas samples from the different power plants. The method detection limits achieved for sample analyses for PCDDs and PCDFs were in the range of 0.1 to 0.7 ng/dscm for the flue gas and combustion air, 0.05 to 0.35 ng/g ash samples, and 1 to 7 ng/liter for aqueous influents and effluents.

SECTION 3

RECOMMENDATIONS

1. Continue the combustion emissions program for other major source categories. The study design principles that were used to assess emissions from coal-fired power plants should be used to obtain emissions information for other source categories. Residential wood combustion and municipal refuse incineration should be high priority categories because of their potentials for emissions of polynuclear aromatic hydrocarbons and polychlorinated aromatics, respectively.

2. Conduct additional analysis of the archived mass spectrometric data from the coal-fired plant samples. The computerized gas chromatography/mass spectrometry data from the present study should be examined to determine the presence of specific compounds in addition to the targeted compounds discussed in this report. It is likely that additional compounds could be identified and semi-quantitated so as to provide a more complete characterization of emissions from coal-fired utility plants.

3. Investigate relationships between emission rates for specific compounds and key plant design and operating parameters. The emissions data contained in this report, plus data generated from additional data interpretation (Recommendation No. 2), should be evaluated with respect to key design and operating parameters employed by the seven plants. Data evaluation via multivariant statistical analysis may provide indications of relationships between specific compound emissions and combustion characteristics.

4. Continue development and evaluation of flue gas sampling systems for quantitative measurement of organic emissions. The modified EPA Method 5 train used for this study efficiently retains particulates and a wide range of organics. However, additional research should be directed toward evaluation and development of adsorbents applicable for a wider range of compounds and with a lower potential for troublesome blanks. Since particulates retained on a heated filter can scavenge or off-gas organics, particulate sampling should be developed which removes the solids from exposure to the gas stream. This would allow reliable determination of organics in both the vaporous and particulate-associated fractions.

5. Develop analytical reference materials for organics in combustion source samples. In particular, standard reference ash samples should be developed with certified concentrations of polynuclear aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans.

SECTION 4

PLANT DESCRIPTIONS

The descriptions of the seven plants and their operating characteristics in this section were obtained from interviews with plant management and operation staff.

PLANT NO. 1

Plant No. 1 consisted of two essentially identical units with capacities of 660 Mw each. The boiler tested, Unit 1, is a pulverized coal-fired furnace, tangentially fired with radiant heat and a balanced draft, divided furnace system. The maximum continuous guaranteed capacity is 5,268,000 lb of steam per hour at the superheater outlet. The boiler is operated in base load with manual control of fuel feed and combustion air. Soot blowing is continuous. Bottom ash removal is continuous during full load and intermittent during partial load, depending on the ash content of the coal.

The coal burned at Plant No. 1 is classified as subbituminous C. The boiler is supplied by eight pulverizer units, each with a rated capacity of 132,000 lb/hr plus 10% overfeed. The design fineness of the coal from the pulverizers is 65% through a No. 200 sieve. The design temperature in the combustion zone is 2500°F (1370°C).

Particulate emissions are controlled by two sets of electrostatic precipitators (ESP) in series. The ESP system consists of primary and secondary fields. The secondary units were added after the initial construction to ensure compliance with federal particulate emission standards. A number of fields in the primary ESP units were inoperable during the test. The flue gases from the secondary ESP units on Boiler No. 1 are discharged via Stack No. 1.

The two secondary ESP units are of the single pass four-field type. Each field is split into six separate bus sections. A high voltage direct current is supplied to the discharge electrodes while the collector electrodes are at ground potential. The discharge electrodes are flattened top mast wire electrodes with 4 x 8 gauge twisted wire elements per mast with four-point suspension. The catch-type collector electrodes are vertical plates fitted at intervals with channel stiffeners.

A continuous chain belt, reducing gear, cam shaft rapping system is used for both the discharge and collector electrode systems. The discharge electrode has drop rod rapping four points per frame. Each collector has two drop rod rapper hammers per plate.

Fly ash is removed from both the primary and secondary precipitator units by an integrated system using the same transport blowers, fly ash bins, and exhausters. Interlocks and valving were installed for sequential loading and unloading of fly ash from the two sets of precipitators connected to the same air and ash piping headers.

PLANT NO. 2

Plant No. 2 consists of five units. Units 1 through 4 have capacities near 250 Mw and are approximately 20 years old. They were originally ducted through individual ESPs into individual stacks approximately 250 ft tall. In recent years, four new ESPs have been installed, and the flue gases have been ducted to a single, dual-flue stack approximately 650-ft tall. Unit 5 has a capacity near 900 Mw and has been in operation for 2 years. It has ESPs and is ducted to a 700-ft stack.

Unit 4 was tested at Plant No. 2. The boiler is a pulverized coal, vertical fired, radiant boiler with a maximum continous high pressure steam output of 1,700,000 lb/hr. The turbine is rated at 250 Mw. The boiler is operated in base load with automatic fuel feed and combustion air control. Soot blowing is intermittent, three times per day. Bottom ash is removed manually about every 3 to 4 hr.

Plant No. 2 burns bituminous coal in 18 burners fed by six pulverizers. Coal is batch weighed. Accurate coal feed data were not available during the test due to a few nonfunctioning integrators in the control room.

Particulate emissions are controlled by electrostatic precipitation. The ESP is operated on the "hot-side" to raise the collection efficiency. In certain types of low sulfur coal, fly ash resistivity is extremely high for the usual operating temperature range (around 250 to 300°F, 120 to 150°C). Higher collection efficiency can be attained by treating the gas at higher temperatures since the resistivity of the fly ash decreases sharply as the temperature increases.

Plant No. 2's ESP system was designed to treat 1,250,000 cfm (cubic feet per minute) of gas entering at 650°F (350°C). The collecting plates in each section are arranged in five groups of six or seven plates each. Suspended in each section are 396 discharge electrode wires. Each section is supplied with power from two rectifier-transformer sets, making a total of eight sets of power control panels for the ESP. The ESP is equipped with 32 ash collection hoppers configured as four rows of eight hoppers each.

The collecting plates are cleaned by 160 magnetic impulse, gravity impact rappers. The discharge electrodes are cleaned by a total of 32 rappers. The switching unit controlling the rappers in each section of the ESP rotates at 1/2 RPM and therefore energizes each rapper once every 2 min.

The bottom ash quenching and boiler seal waters are not recycled in the plant, and the overflows go into a single sink-type drain. Boiler makeup water is taken from a nearby river.

PLANT NO. 3

Plant No. 3 is comprised of three essentially identical units rated at 125 Mw each. They are typically operated at 120 Mw, burning approximately 45 tons of coal per hour. The units are operated as low as 40 Mw each on weekends.

Unit No. 3 was tested at Plant No. 3. This boiler was placed into operation during 1951-1952 using cyclone dust collectors to control particulate emissions. The cyclones were taken out of service and replaced with dry electrostatic precipitators in 1973-1974. The unit is front wall fired with eastern Kentucky coal which has a heating value of approximately 12,000 Btu/lb. The coal typically contains 10 to 15% ash. The ash is distributed as approximately 90% fly ash and economizer ash and 10% bottom ash.

The boiler is operated at base load. Fuel feed and combustion air are automatically controlled but can also be operated manually. Four pulverizers serve each boiler. These crush the coal to powder consistency by rolling large steel rollers over the coal. The pulverized coal is then fed to the burners. Coal feed rate to the boiler is regulated by adjusting the amount of coal fed to the pulverizers. This rate usually varies according to the heat content of the coal and the quantity of output required from the turbine. Coal loading is based on totals for a 24-hr day. The calibrators for each pulverizer were not operating during the test.

Soot blowing occurs once per shift. Bottom ash is sluiced out of the collection hoppers once per shift. Ash collected by the ESP is continuously removed to a recovery station.

The ESP that serves Boiler No. 3 was constructed by American Standard and placed in operation in 1973-1974. It is a high voltage, single-stage system that replaced cyclone dust collectors. The ESP ash collection system is comprised of two rows of four hoppers each. The first row removes 70 to 80% of the ash. Total collection efficiency was 99.96% during the latest compliance test.

PLANT NO. 4

Plant No. 4 consists of five identical units rated at 217 Mw. They were installed in 1954-1955 and were originally ducted into three stacks approximately 400 ft tall. During 1980, ESPs were installed and all boilers were ducted into a single 1,000-ft stack.

Unit No. 2 was tested at Plant No. 4. The boiler is a pulverized coal-fired, radiant, front wall fired system with a steam capacity of 1,336,000 lb/hr. The turbine has a nameplate total net generation capacity of 207 Mw. The boiler is operated in peak load with automatic fuel feed and manual combustion air control. Soot blowing and bottom ash removal are intermittent once per shift.

The coal burned at Plant No. 4 is a bituminous coal. Seven pulverizers are available for Unit No. 2. Specific coal feed weight values were not available.

An ESP with multiple sections single casing construction is located in the gas duct between the air preheater and the common stack. The ESP is designed to handle a gas volume of 925,000 CFM at an average bulk flue gas temperature of 350°F (175°C) with inlet grain loading ranging from 0.5 to 3.5 g/ft^3.

The ESP consists of five fields arranged in series in the direction of gas flow. Each field has four bus sections, resulting in a total of 20 bus sections, each a rigid boxlike structure. The discharge electrodes are stainless steel wires suspended vertically in 28 parallel rows. The collecting plates are 16-gauge steel plates.

The rapping systems for both the discharge electrodes and the collecting plates are "tumbling hammers" mounted on horizontal shafts in a staggered manner. The operation of the gear motors for the rapper system is controlled by a program relay which can be adjusted to optimize the performance of each bus section. Fly ash is collected in 20 hoppers, each suspended below a bus section structure.

PLANT NO. 5

Plant No. 5 consists of a single unit with a net operating capacity of 584 Mw. The unit is cyclone-fired with eastern bituminous coal supplied by five pulverizer mills. The mills are rated at more than 70 tons/hr (63,500 kg/hr) and are designed for removal of pyrites. At full capacity, the boiler delivers 4,000,000 lb of steam per hour to a four flow, single reheat turbine. The unit is operated at base load using automatic fuel feed and automatic combustion air control. Soot blowing is continuous and bottom ash is typically removed twice per 8-hr shift. The unit operates near capacity during the day. The output is typically reduced to 450 to 480 Mw for a few hours each evening. Approximately 40% of the power produced services industrial users.

Particulate emissions are controlled by two electrostatic precipitators (ESPs). One ESP is located at each preheater gas outlet. Each ESP consists of four units with three fields. The two ESPs were designed to treat 1,984,000 cfm (56,180 cmm) of gas at 270°F (130°C).

Each precipitator contains 360 collecting plates (30 x 9 ft, or 9.1 x 2.7 m) and 4,176 discharge electrodes (0.109 in., or 2.8 mm, copper Bessemer wires supporting a 25-lb, or 11.3 kg, plumb bob). Power is supplied to each ESP from six rectifier-transformers. Collected ash is removed from the plates and discharge electrodes by magnetic impulse, gravity impact rappers (six per section for plates and two per section for electrodes) energized at 2-min intervals. Ash is collected in 12 hoppers and slurried for disposal.

PLANT NO. 6

Plant No. 6 consists of three units with capacities of 180, 290, and 670 Mw. Unit 1 (180 Mw) was tested. Unit 1 (in operation ∿ 15 years) is cyclone-fired and is operated primarily in base load with automatic fuel feed and automatic combustion air control. The unit burns bituminous coal. Soot blowing is intermittent (approximately one cycle per shift). Bottom ash is typically removed at 2- to 4-hr intervals.

The ESP system consists of two fields with four collection hoppers each. Because of their age, the ESP was not operating efficiently during the test. Addition of a new system was in progress.

PLANT NO. 7

Plant No. 7 consists of five units. Units 1, 2, and 3 are natural-gas-fired boilers used for peak load power. Units 4 and 5 are coal-fired boilers operated in base load. Unit 5 was tested. Unit 5 has a maximum gross capacity of 580 Mw. It is cyclone-fired and is operated at base load with automatic fuel feed and automatic combustion air control. The unit burns bituminous coal and is fed by six pulverizer mills rated at more than 35 tons/hr (31,800 kg/hr) each. Soot blowing is continuous. Bottom ash is typically removed once each shift. Particulate emissions are controlled by two electrostatic precipitator units in parallel.

SECTION 5

SAMPLING METHODS

The general procedures for sampling the gaseous, solid, and aqueous emissions from each of the four different coal-fired power plants are described in the methods manual in Appendix A. Flue gas samples (20 m^3) were collected at each plant with two modified Method 5 organic sampling trains operating simultaneously (see Figure 1; Appendix A). Plant background air was collected using an XAD-2 resin cartridge. The solid and aqueous grab samples were collected according to specific schedules provided by RTI for random sampling at each plant. The sampling schedules were dependent on the number of available sampling points, such as the number of ash hoppers, and the wasting schedules of the normal plant operations.

The specific sampling procedures were modified as required by the design of each plant and the accessibility of sampling sites. For example, the flue gas at Plant Nos. 1, 3, and 5 was sampled with the probe attached directly to the sample box in a conventional horizontal sampling position. Plant Nos. 2 and 4 required vertical sampling and included a heated flexible line between the sample probe and the modified Method 5 train. A heated flexible line was also used to facilitate horizontal sampling at Plant Nos. 5 and 7. Flue gas sampling at Plant No. 2 required the use of a tripod assembly to hold the probe in the horizontal position. The sample probe used at Plant No. 4 (shown in Figure 1) was 25 ft in length and was lined with polytetrafluoroethylene (TFE). A special sampling scaffold and probe suspension device was constructed to provide safe access to the sample ports and to aid probe handling operations with overhead pulley controls.

Other specific differences in sampling at the four plants involved minor operational changes for the modified Method 5 sampling train. The ball joints for the sampling train used at Plant No. 1 were sealed with glycerol. However, the sealant tended to evaporate from joints in the heated zones so that frequent reapplication of the sealant was required to avoid leaks. Thereafter, DC-200, a high temperature silicon phase, was used to seal the joints in Plant Nos. 2, 3, and 4. Also, the high temperature silicon gaskets used in the filter housings for the sampling trains at Plants 1 and 2 were replaced with TFE gaskets for Plants 3 and 4 to reduce possible contamination from gasket materials.

Also, Apiezon L was used to seal all spherical joints on trains used at Plant Nos. 5, 6, and 7. The sealant was easily removed from the joints with a clean tissue saturated with cyclohexane just prior to rinsing each component during sample recovery.

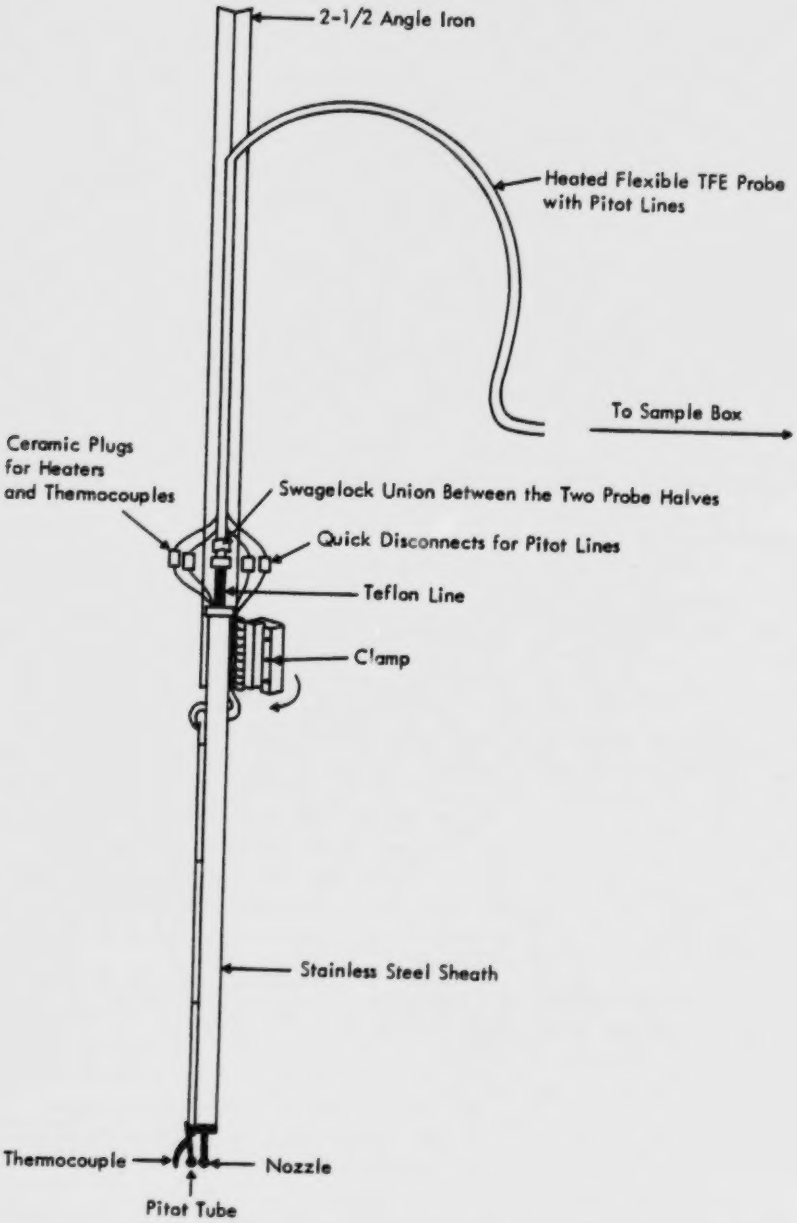

2-1/2 Angle Iron
Heated Flexible TFE Probe with Pitot Lines
To Sample Box
Ceramic Plugs for Heaters and Thermocouples
Swagelock Union Between the Two Probe Halves
Quick Disconnects for Pitot Lines
Teflon Line
Clamp
Stainless Steel Sheath
Thermocouple
Nozzle
Pitot Tube

Figure 1. Flue gas sampling probe used at Plant No. 4.

FLUE GAS TRAIN EVALUATION

The collection efficiency of the flue gas sampling train was evaluated for several target compounds by sampling spiked laboratory air. Complete trains (without pilot tubes and sampling probes) were assembled (using Apiezon L sealant) and operated in the laboratory in a manner simulating actual flue gas sampling, i.e., operated for ~ 8 hr at sampling rates ranging from 0.70 to 0.80 ft^3/min with the filter box at 275°F and ice water cooling of impingers, condenser, and resin cartridge.

Trains were spiked using a special spike probe. The spike probe, shown in Figure 2, was fitted to the train with the hole on top and the dimple on the bottom. Small aliquots of spiking solutions were deposited in the dimple by syringe via the hole. The spike probes were then heated with a heat gun to volatilize the spike into the gas stream during sampling. At the conclusion of each run, the sample was recovered from the train, excluding the spike probe, and analyzed as described in Section 6. The spike probe was thoroughly rinsed with acetone and cyclohexane and the combined rinses analyzed in the same fashion.

A total of seven tests were conducted. These included a blank run and six spiked runs. The spiked runs were spiked with aliquots of one solution from each of three pairs of solutions. The total volume of solutions for each test run was 250 µl. The solutions pairs contained low and high concentrations of PAH and miscellaneous compounds, PCBs (Aroclor 1254), and selected PCDDs. The selection scheme for the train test runs is shown in Table 1.

The results of the train evaluation tests are summarized in Table 2. The total recoveries were generally good for all compounds except 1,2,4-trichlorobenzene and 2,4,6-trichlorophenol. Total recoveries in excess of 100% were found from the low level spikes for some compounds, notably chrysene, 2-chlorodibenzo-p-dioxin, and 2,7-dichlorodibenzo-p-dioxin.

In general, a larger fraction of the total recovery for less volatile compounds was found on the spike probe. This trend was observed before analysis for tetra- through hexachlorobiphenyls and 1,2,3,4-tetrachlorodibenzo-p-dioxin was completed. In order to reduce the analytical effort, those compounds were not determined in the train extracts.

The precisions of the total recovery determinations were also generally good. The much larger variability observed for recoveries for several compounds from the spike probes and trains likely reflect run-to-run variations in the fraction of the spike volatilized into the gas stream. Nonetheless, the results of the collection efficiency tests demonstrate the applicability of the modified EPA Method 5 train for organics sampling.

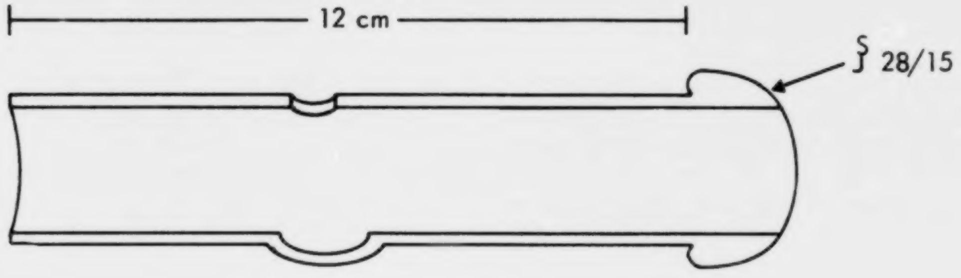


Figure 2. Flue gas train evaluation spiking probe.

TABLE 1. SPIKING SOLUTION SELECTION SCHEME FOR FLUE GAS TRAIN EVALUATION TESTS

Spike test no.	PAH and misc.		PCBs		PCDDs	
	Low conc.	High conc.	Low conc.	High conc.	Low conc.	High conc.
1	X			X		X
2		X	X			X
3	X			X	X	
4		X		X	X	
5		X	X		X	
6	X		X			X

TABLE 2. RESULTS OF FLUE GAS TRAIN EVALUATIONS

Compound	Spike level (µg)	Recovery (%)		
		Probe	Train	Total
Naphthalene	100	ND[a]	76 ± 5[b]	76 ± 5[c]
	1,000	ND	61 ± 6	61 ± 6
1,2,4-Trichlorobenzene	273	ND	26 ± 4	26 ± 4
	2,730	ND	51 ± 6	51 ± 6
2,4,6-Trichlorophenol	252	ND	10 ± 4	10 ± 4
	2,520	0.1 ± 0.2	33 ± 7	33 ± 7
Di-n-butylphthalate	250	19 ± 22	35, 42[d]	35, 85[d]
	2,500	47 ± 8	30 ± 10	77 ± 7
Di-n-octylphthalate	265	72, 79[d]	5 ± 9	72, 95[d]
	2,650	96, 75[d]	ND	96, 75[d]
Chrysene	115	140 ± 18	15 ± 16	150 ± 8
	1,150	81 ± 19	ND	81 ± 19
Aroclor 1254	110.6			
Trichlorobiphenyls (4)[e]		75 ± 15	24 ± 21	98 ± 22
Tetrachlorobiphenyls (5)		89 ± 24	NA[f]	89 ± 24
Pentachlorobiphenyls (3)		87 ± 19	NA	87 ± 19
Hexachlorobiphenyls (4)		99 ± 25	NA	99 ± 25
	1,106			
Trichlorobiphenyls (4)		51 ± 28	39 ± 29	90 ± 12
Tetrachlorobiphenyls (5)		93 ± 17	NA	93 ± 17
Pentachlorobiphenyls (3)		68 ± 10	NA	68 ± 10
Hexachlorobiphenyls (4)		71 ± 8	NA	71 ± 8
2-Chlorodibenzo-p-dioxin	1.0	ND	210 ± 21	210 ± 21
	10	9 ± 12	95 ± 42	100 ± 30
2,7-Dichlorodibenzo-p-dioxin	1.0	13 ± 23	140 ± 40	150 ± 50
	10	36 ± 33	61 ± 41	97 ± 9

(continued)

TABLE 2 (continued)

Compound	Spike level (μg)	Recovery (%)		
		Probe	Train	Total
1,2,7-Dichlorodibenzo-p-dioxin	1.0	63 ± 18	66 ± 31	130 ± 17
	10	43 ± 36	45 ± 40	88 ± 5
1,2,3,4-Tetrachlorodibenzo-p-dioxin	1.0	100 ± 18	NA	100 ± 18
	10	61, 81[d]	NA	61, 81[d]

[a] ND = not detected.

[b] Mean ± standard deviation for three tests.

[c] Since mean total recoveries were calculated from total recoveries of individual tests, mean total recoveries may not equal sum of the mean components recoveries due to rounding.

[d] Results for two determinations. One analysis was an obvious outlier.

[e] Pooled recovery results for number of chromatographic peaks in parenthesis.

[f] NA = not analyzed. Total recovery represents amount in spike probe only.

SAMPLING LOCATIONS, PLANT NO. 1

The samples collected from each plant are summarized in Table 3 with the corresponding collection frequencies and descriptions of typical sampling points. A more detailed discusson of the specific sampling locations and grab sampling methods used at each plant is given below.

Flue Gas Outlet

Four ports were located on the stack at the 220-ft level. Figure 3 shows a schematic representation of the traverse point locations on the stack. A heated, flexible, TFE line was used to connect the glass-lined probe to the sample box to allow maneuverability in the limited space between the concrete shell and the steel stack. Table 4 lists the sampling points relative to the distance from the inside wall and fraction of the stack internal diameter. Figure 3 also shows the exact location of the sample ports on the stack and the position of the continuous monitoring equipment.

ESP Ash

ESP ash from both units at Plant No. 1 was conveyed to a storage bin prior to loading into trucks for disposal. A portion of the ash was removed from the bin to a size classifier prior to sale as a cement aggregate. Since no access was available for sampling ash between the ash collection hoppers and the storage bin, samples were taken from the air slide that conveys ash from the bin to the classifier. Hence, the ESP ash samples from Plant No. 1 contain ash from both units.

Bottom Ash

Bottom ash was sluiced from Unit No. 1 to two holding bins (designated 11 and 12). The ash was dewatered by sedimentation prior to loading into trucks for disposal. The dewatered ash was sampled with a scoop as it was dumped into the trucks.

Waters

Bottom ash hopper quench water was sampled from an overflow tank adjacent to the bottom ash hopper. Influent water was sampled from a tap near the hopper. Raw plant makeup water was sampled from a tap in the pump house.

Coal

Coal was sampled from conveyers feeding bunkers for both units at Plant No. 1. Samples were taken at 2-hr intervals, ground, and combined into daily composites by the plant staff.

TABLE 3. SAMPLES COLLECTED, SAMPLING LOCATIONS, AND COLLECTION FREQUENCIES

Sample type Gaseous samples	Typical location	Collection frequency
Gaseous samples		
1. Flue gas	Ports on stack or duct downstream of ESP	1/day (20 m^3)
2. Plant background air	Near forced draft fans	1/day (10 m^3)
Solid samples		
1. Coal	Feed streams between bunker(s) and pulverizer mills	6/day
2. Bottom ash	Collection hopper or sluice line	6/day
3. Fly ash	Individual hoppers or pneumatic waste line	6/day
Aqueous samples		
1. Quench water effluent	Overflow from bottom ash hopper or sluice line	3-6/day
2. Quench water	Tap near bottom ash hopper	1-3/day

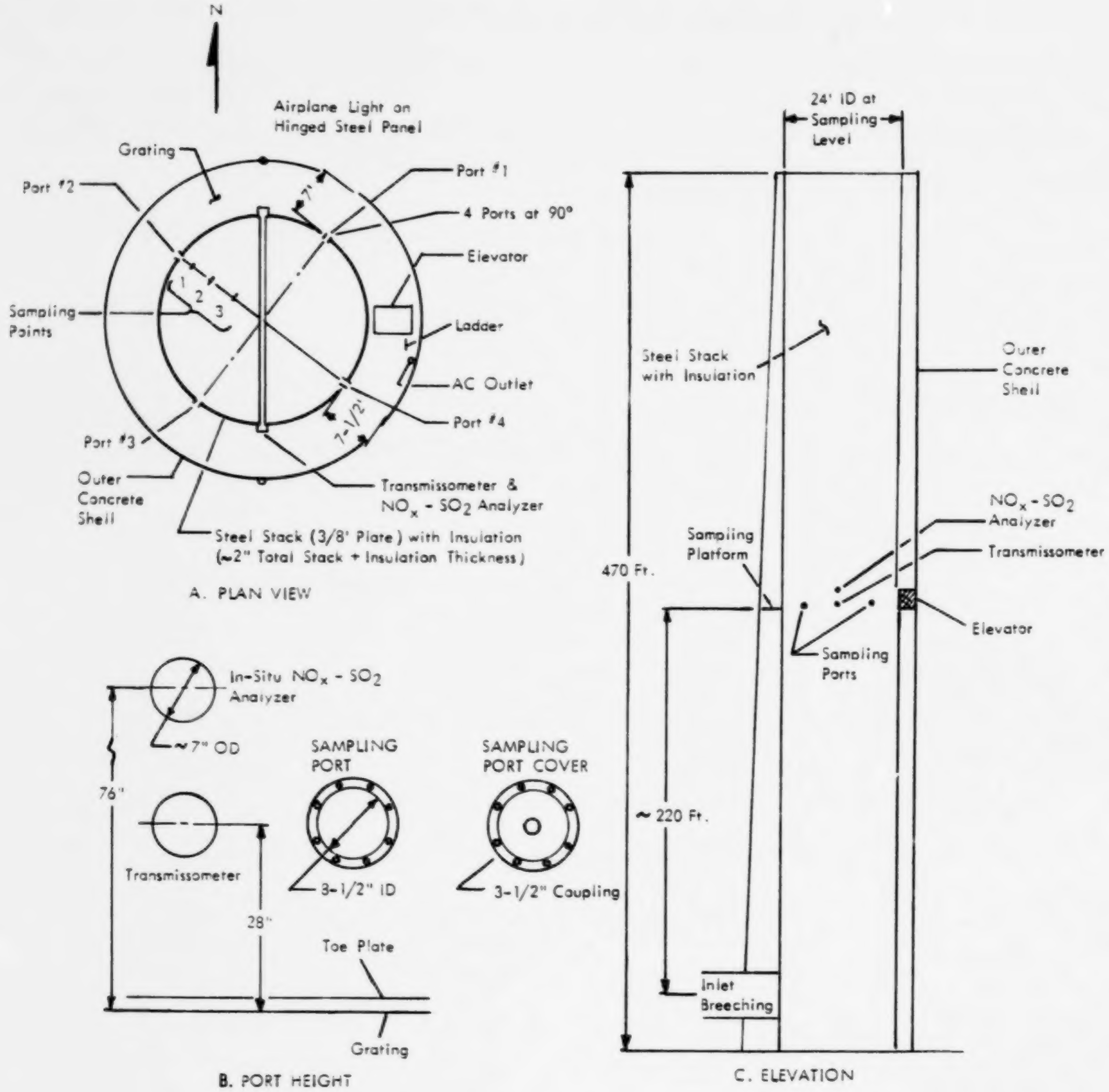

N
Airplane Light on Hinged Steel Panel
Grating
Port #2
Port #1
7"
4 Ports at 90°
Elevator
Sampling Points
1
2
3
Ladder
AC Outlet
7-1/2"
Port #4
Port #3
Outer Concrete Shell
Transmissometer & NO_x - SO_2 Analyzer
Steel Stack (3/8" Plate) with Insulation (~2" Total Stack + Insulation Thickness)
A. PLAN VIEW
In-Situ NO_x - SO_2 Analyzer
~7" OD
76"
Transmissometer
SAMPLING PORT
3-1/2" ID
SAMPLING PORT COVER
3-1/2" Coupling
28"
Toe Plate
Grating
B. PORT HEIGHT
24' ID at Sampling Level
Steel Stack with Insulation
Outer Concrete Shell
NO_x - SO_2 Analyzer
Transmissometer
Sampling Platform
470 Ft.
Elevator
Sampling Ports
~ 220 Ft.
Inlet Breeching
C. ELEVATION

Figure 3. Schematic representation of the flue gas sampling location from: (A) plan as cross-sectional view; (B) port height; and (C) with respect to stack elevation for Plant No. 1.

TABLE 4. MODIFIED METHOD 5 TRAIN SAMPLE POINT LOCATIONS, PLANT NO. 1

Radius point	Fraction of duct ID (%)	Distance from inside wall (in.)
1	4.4	12.6
2	14.6	42.0
3	29.6	85.3

Plant Background Air

Plant background air was sampled on the ground floor near the forced-draft fans.

Continuous Monitoring

A port for continuous monitoring was available on the duct inlet to the primary ESP system.

SAMPLING LOCATIONS, PLANT NO. 2

Flue Gas Outlet

Sixteen ports were located on the duct outlet to the ESP under eight deck plates between the first two rows of ESP hoppers. The ports were approximately 2 ft below the floor level and were canted approximately 10 degrees from vertical. The duct was approximately 5 ft deep at the ports. The location of the sampling ports for Plant No. 2 are shown in Figures 4 to 6. Figure 7 shows the locations of the traverse points.

ESP Ash

The ESP hopper array, consisting of four rows of eight hoppers, is illustrated in Figure 8. Ash was removed via a valve at the bottom of each hopper. RTI constructed a hopper selection and sampling schedule to obtain six samples per day. Each sample consisted of fly ash from one hopper from each row. Extreme caution was exercised in taking these samples. The ESPs were "hot-side" so that the ash was typically 400-500°F (200-260°C).

Bottom Ash

Bottom ash was wasted twice per shift. Just prior to wasting, the operator drew down the quench water and opened a hatch to allow removal of a sample with a long handle shovel. Samples were taken from specific sectors from the two ends of the hopper according to a selection scheme provided by RTI. Figure 9 shows the sector locations.

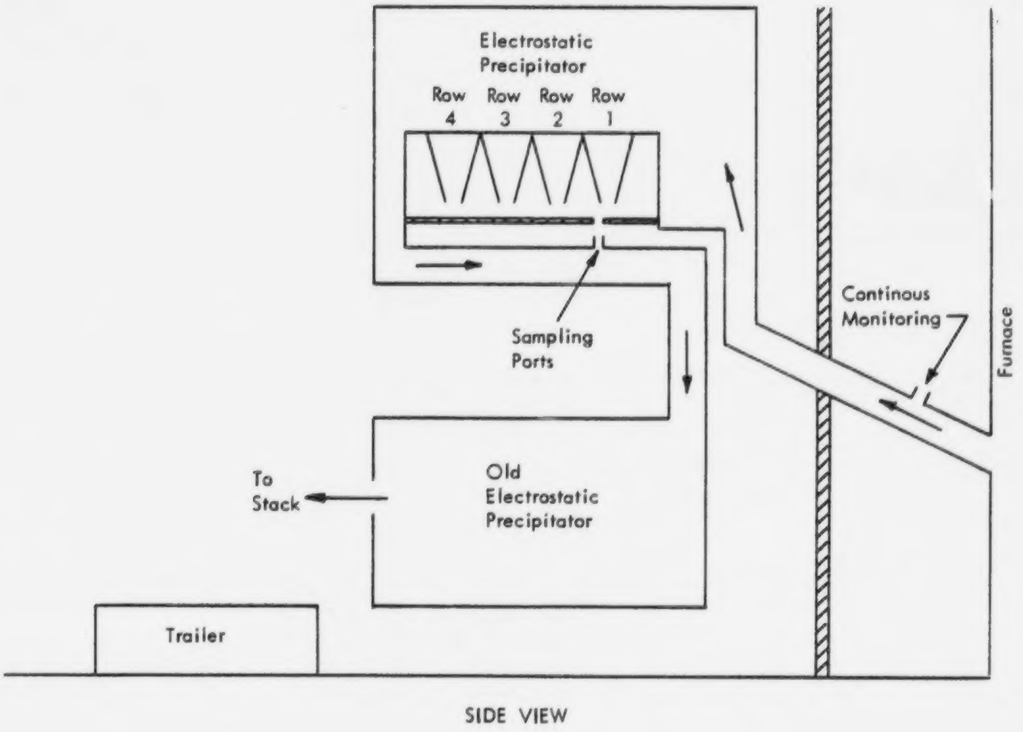

Electrostatic Precipitator
Row 4
Row 3
Row 2
Row 1
Sampling Ports
Continous Monitoring
Furnace
To Stack
Old Electrostatic Precipitator
Trailer
SIDE VIEW

Figure 4. Locations of flue gas inlet and continuous monitoring sampling sites, Plant No. 2.

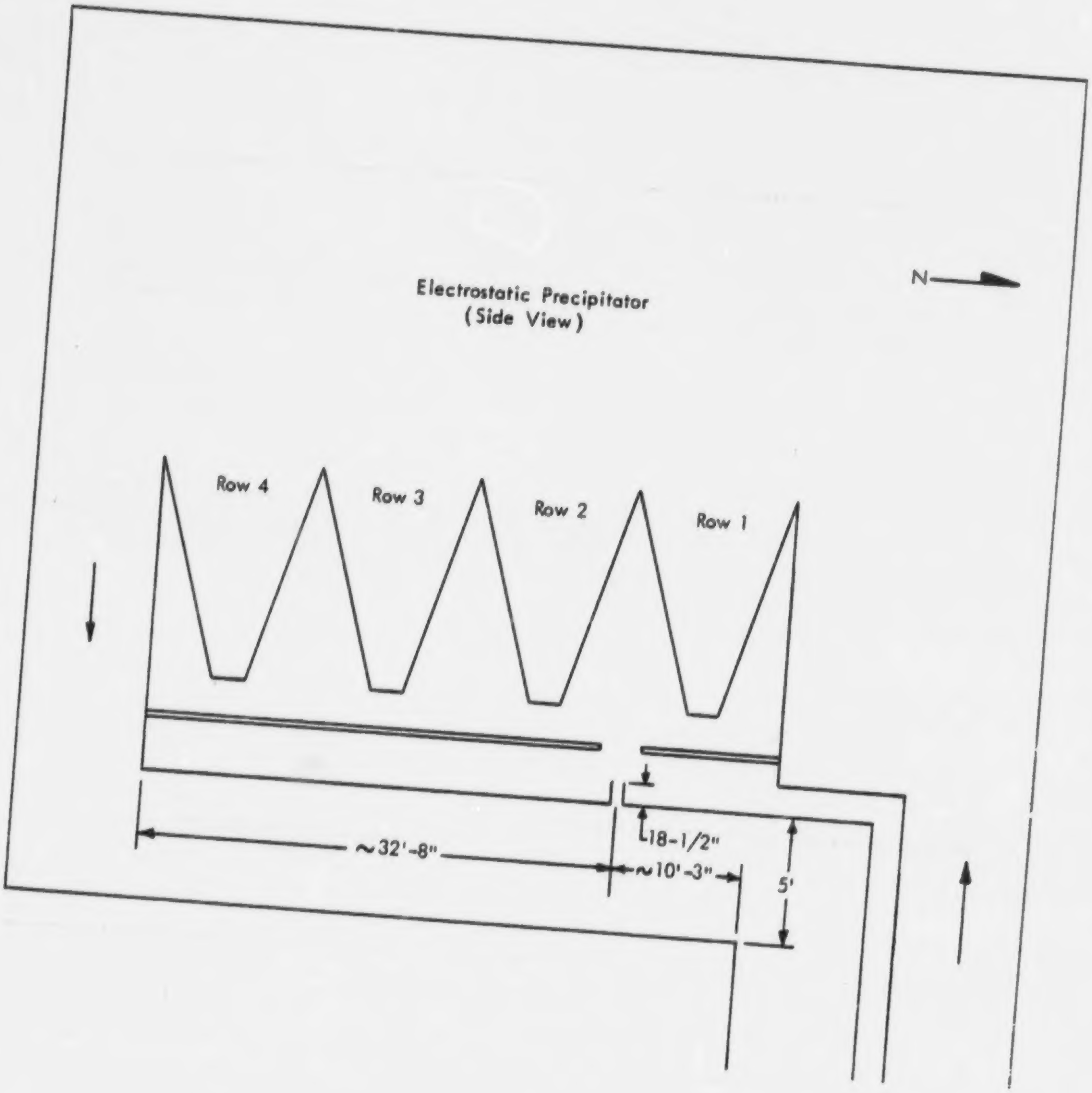

Electrostatic Precipitator
(Side View)
N
Row 4
Row 3
Row 2
Row 1
18-1/2"
~32'-8"
~10'-3"
5'

Figure 5. Side view of the ESP, Plant No. 2.

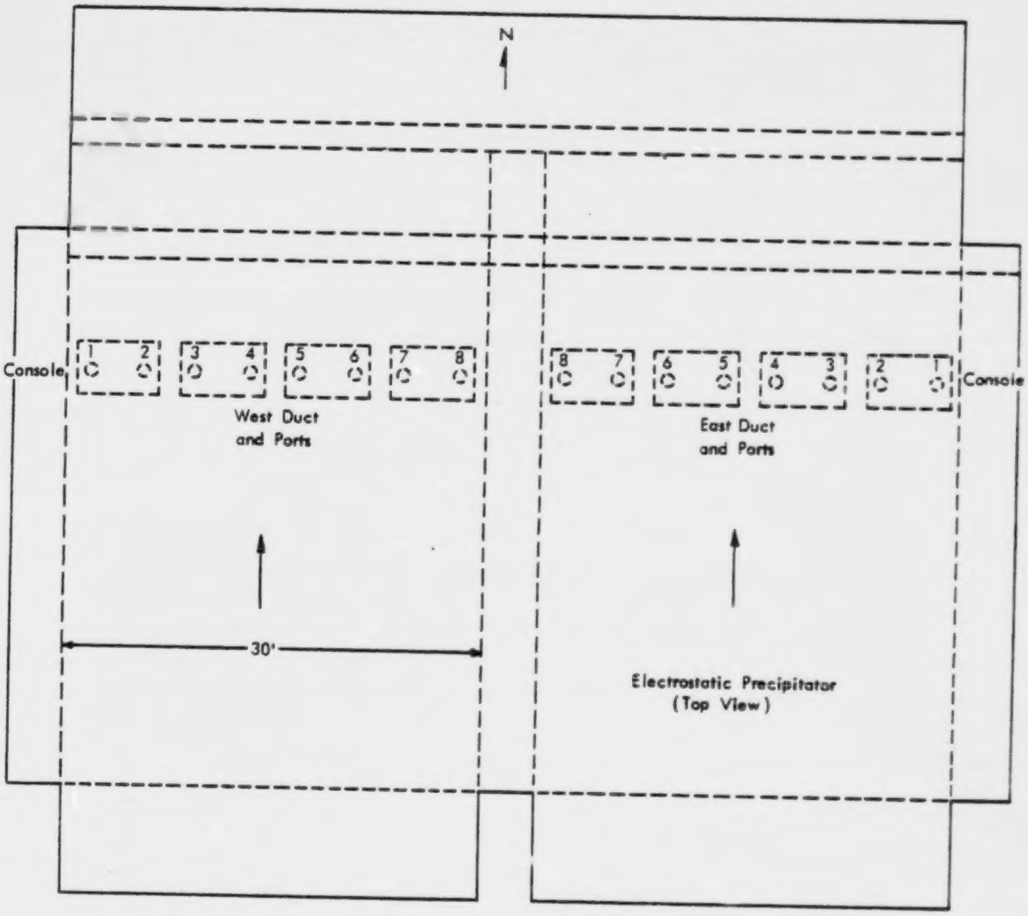
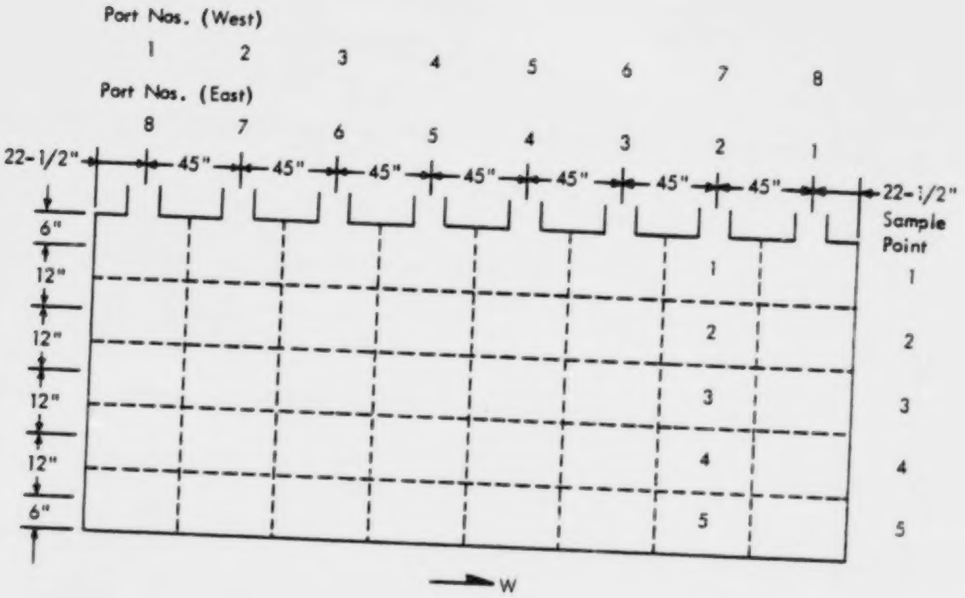

N
Console
1
2
3
4
5
6
7
8
West Duct and Ports
8
7
6
5
4
3
2
1
Console
East Duct and Ports
30'
Electrostatic Precipitator (Top View)

Figure 6. Top view of the ESP and sampling ports, Plant No. 2.


Port Nos. (West)
1 2 3 4 5 6 7 8
Port Nos. (East)
8 7 6 5 4 3 2 1
22-1/2"
45"
22-1/2"
Sample Point
1
2
3
4
5
6"
12"
12"
12"
12"
6"
W

Point No.	Distance from Inside Wall (in.)
1	6"
2	18"
3	30"
4	42"
5	54"

Figure 7. Traverse points at each sampling port for isokinetic sampling, Plant No. 2.

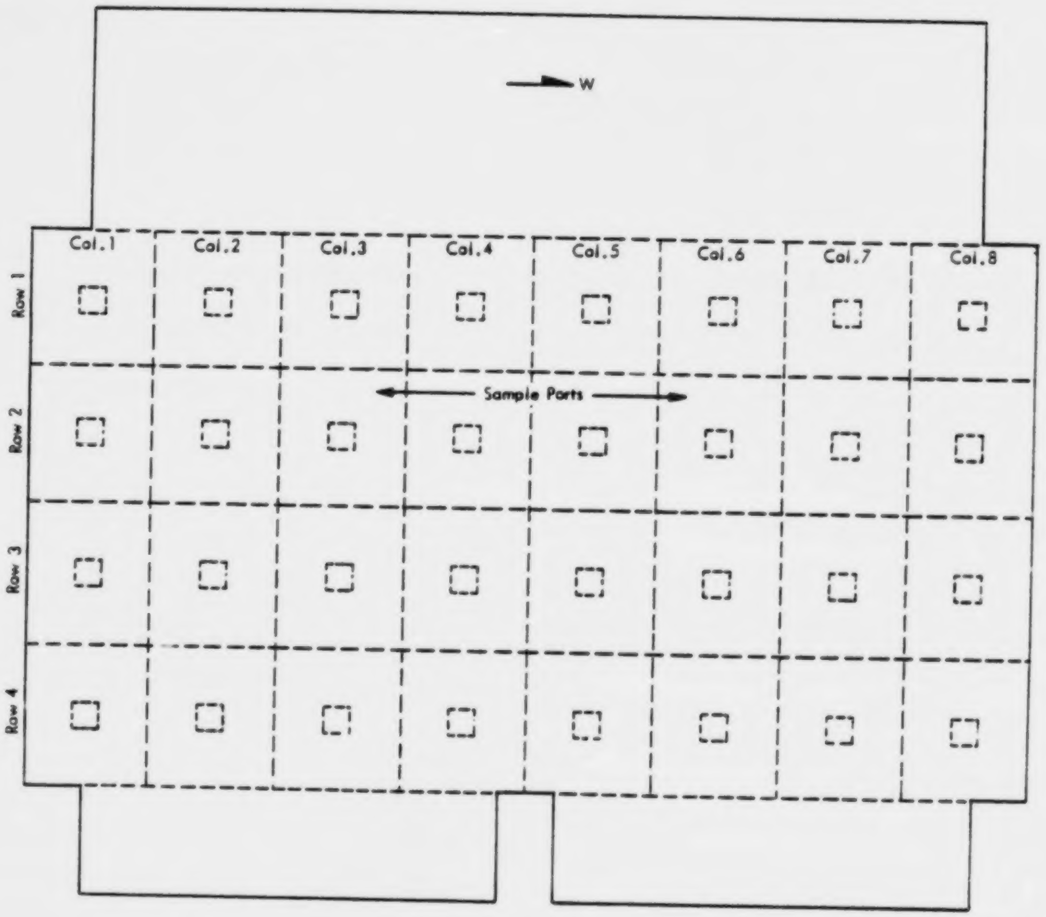

W
Col. 1
Col. 2
Col. 3
Col. 4
Col. 5
Col. 6
Col. 7
Col. 8
Row 1
Row 2
Row 3
Row 4
Sample Ports

Figure 8. Top view of the fly ash hoppers, Plant No. 2.

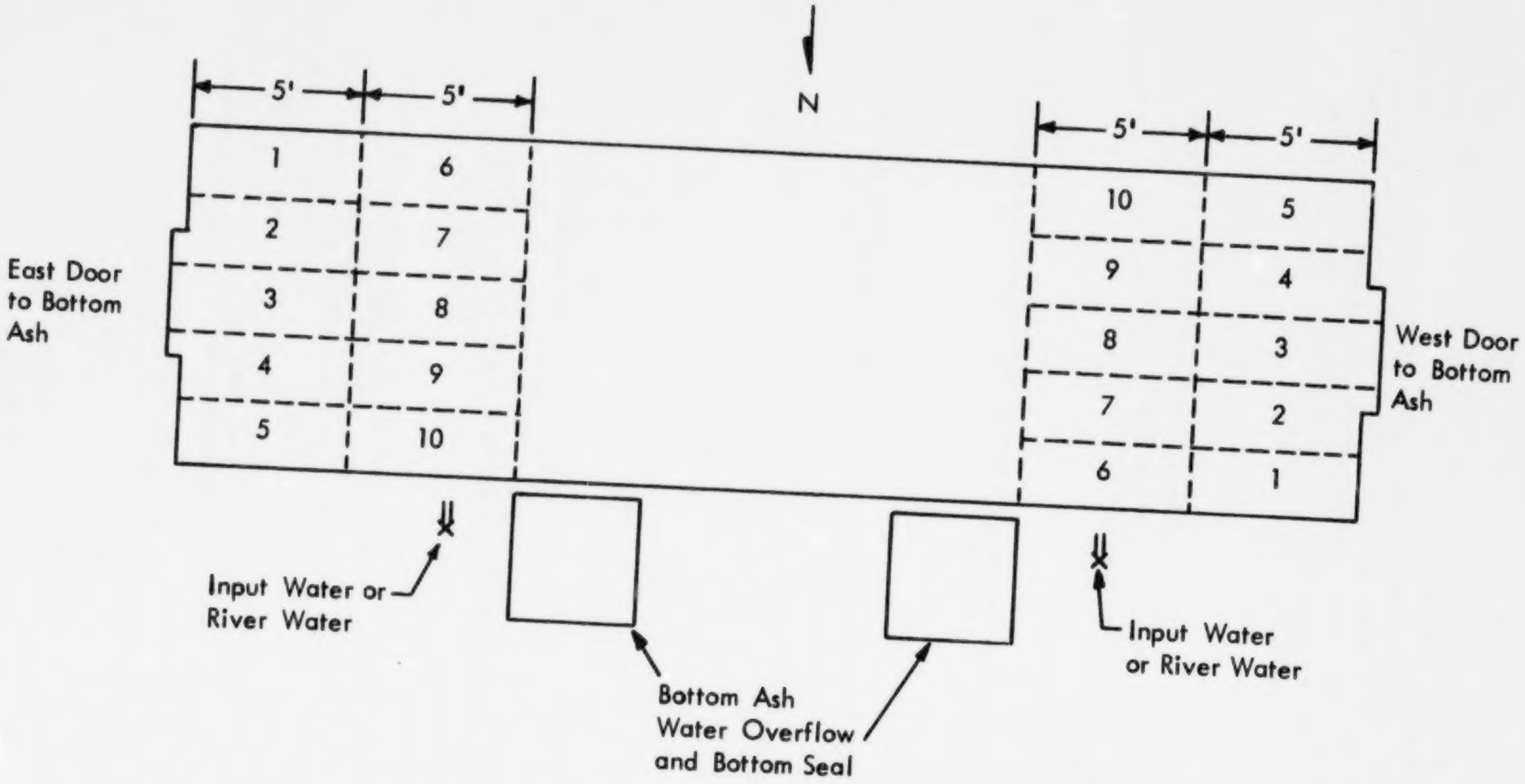

5'
5'
N
5'
5'
1
2
3
4
5
6
7
8
9
10
10
9
8
7
6
5
4
3
2
1
East Door to Bottom Ash
West Door to Bottom Ash
Input Water or River Water
Bottom Ash Water Overflow and Bottom Seal
Input Water or River Water

Figure 9. Bottom ash hopper and water sampling sites, Plant No. 2.

Waters

The bottom ash quenching and boiler seal waters were not recycled. The quench overflow and boiler seal overflowed into a single sink-type drain and were sampled by simple bottle immersion. The quench overflow cascaded from a 6-8 in. pipe and was warm to the touch. The boiler seal water flowed from a 2-3 in. pipe and was cool. Makeup water was drawn from a nearby river and was taken from a tap near the overflow basin. The sampling locations for waters are also indicated on Figure 9.

Coal

The boilers were fired with pulverized coal. The coal was sampled from the six weighing tables just above each pulverizer. The coal was typically about 1/4 in. (6 mm) at this point with a few pieces as large as 3/4 in (20 mm).

Plant Background Air

Plant background air was sampled near the forced draft fans on an upper level in the plant building.

Continuous Monitoring

A port for continuous monitoring was available on the duct just ahead of the ESP. The port location is indicated in Figure 4.

SAMPLING LOCATIONS, PLANT NO. 3

Flue Gas

Eight horizontal ports were located on the duct between the ESP and the stack. Figures 10 and 11 show side and top views of the ducts and the port locations. The sampling platform was directly accessible from the top floor of the plant building. The flue gas was sampled isokinetically such that approximately 20 m^3 of flue gas was collected between two modified Method 5 sampling trains. Figure 12 shows the locations of the traverse points on a horizontal cross-section of the outlet duct.

ESP Ash

The ESP ash collection system was comprised of two rows of four hoppers each. The first row removed 70 to 80% of the ash. The total efficiency of the ESP system was 99.96% at the last compliance test. Ash was sampled directly from the valves on the hoppers. A pipe fitting and adaptor were used to collect hot fly ash from the valve. RTI constructed a hopper selection schedule to obtain a sample from each of the two rows of hoppers six times per day. Figure 13 illustrates the ESP hopper arrangement for Unit No. 3 at Plant No. 3.

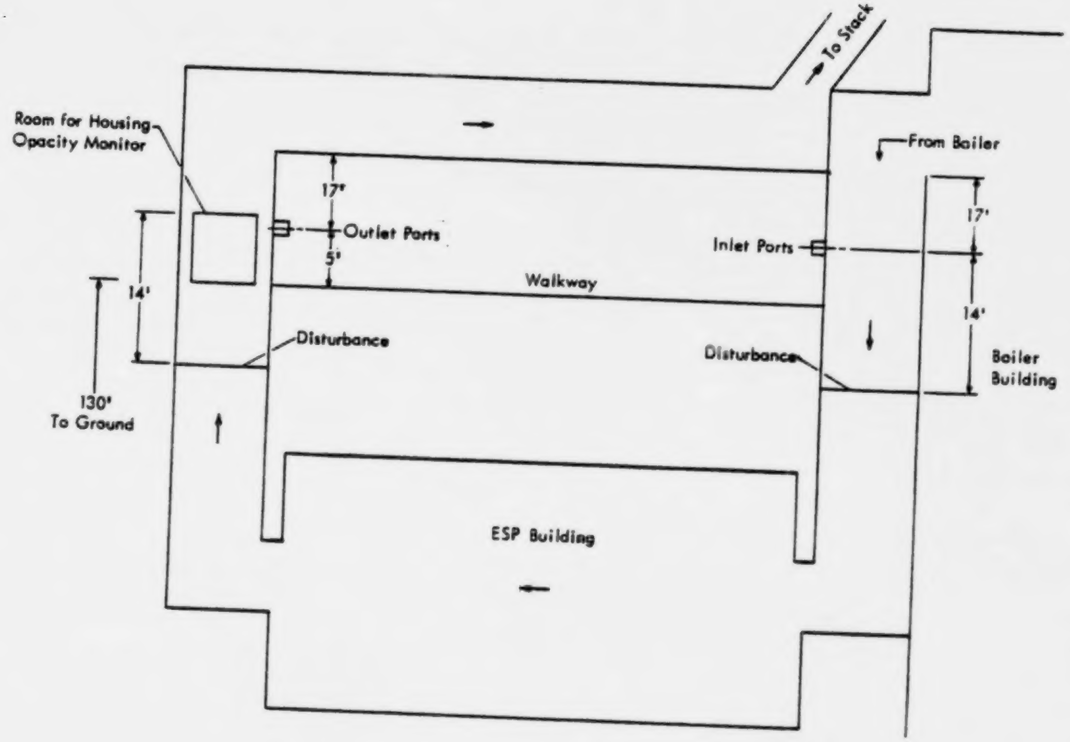

To Stack
Room for Housing Opacity Monitor
From Boiler
17'
Outlet Ports
5'
Inlet Ports
17'
14'
Walkway
14'
14'
Disturbance
Disturbance
Boiler Building
130' To Ground
ESP Building

Figure 10. Side view of the flue gas outlet duct and disturbance points, Plant No. 3.

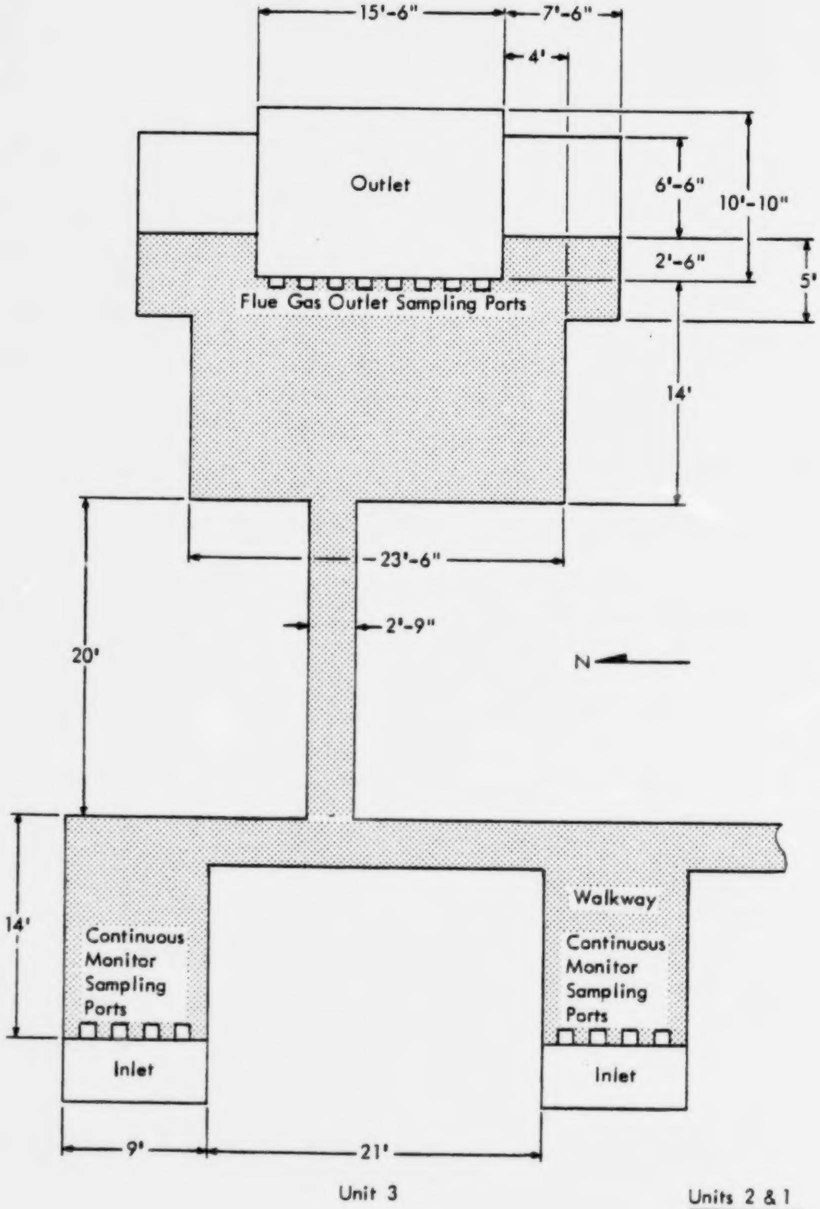

15'-6"
7'-6"
4'
Outlet
6'-6"
10'-10"
2'-6"
5'
Flue Gas Outlet Sampling Ports
14'
23'-6"
2'-9"
20'
N
14'
Walkway
Continuous Monitor Sampling Ports
Continuous Monitor Sampling Ports
Inlet
Inlet
9'
21'
Unit 3
Units 2 & 1

Figure 11. Top view of the sampling platform above the vertical ducts, Plant No. 3.

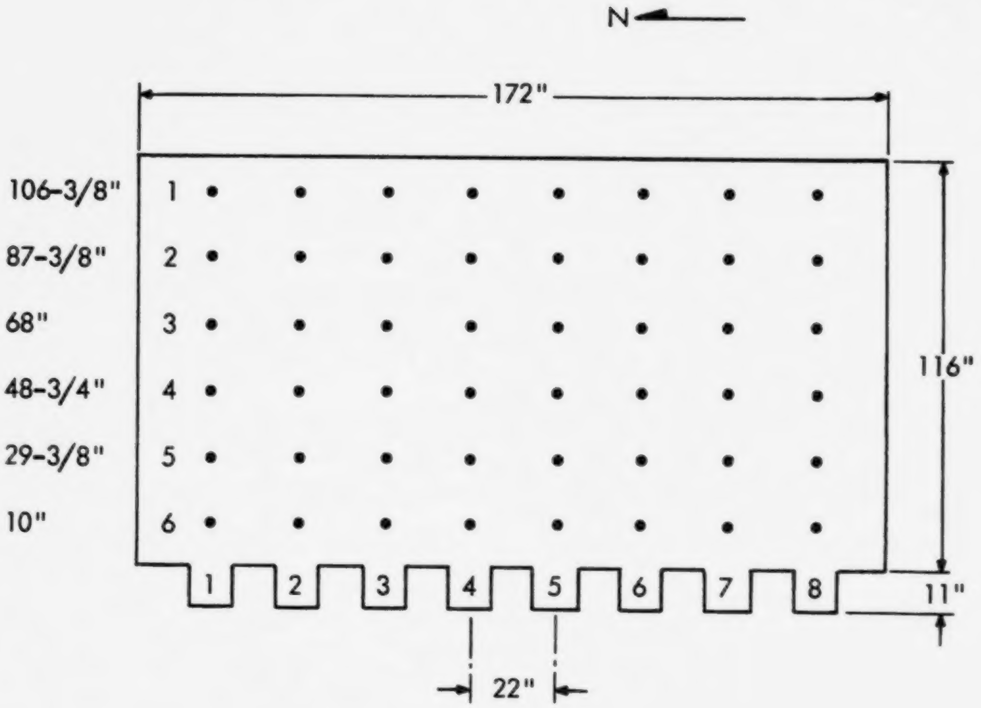

N
172"
106-3/8"
87-3/8"
68"
48-3/4"
29-3/8"
10"
1
2
3
4
5
6
116"
1
2
3
4
5
6
7
8
11"
22"

Figure 12. Location of sampling ports and individual sampling points for isokinetic sampling within the flue gas outlet duct, Plant No. 3.

*NOTE: These measurements are taken from the inside wall, excluding the length of the nipple.

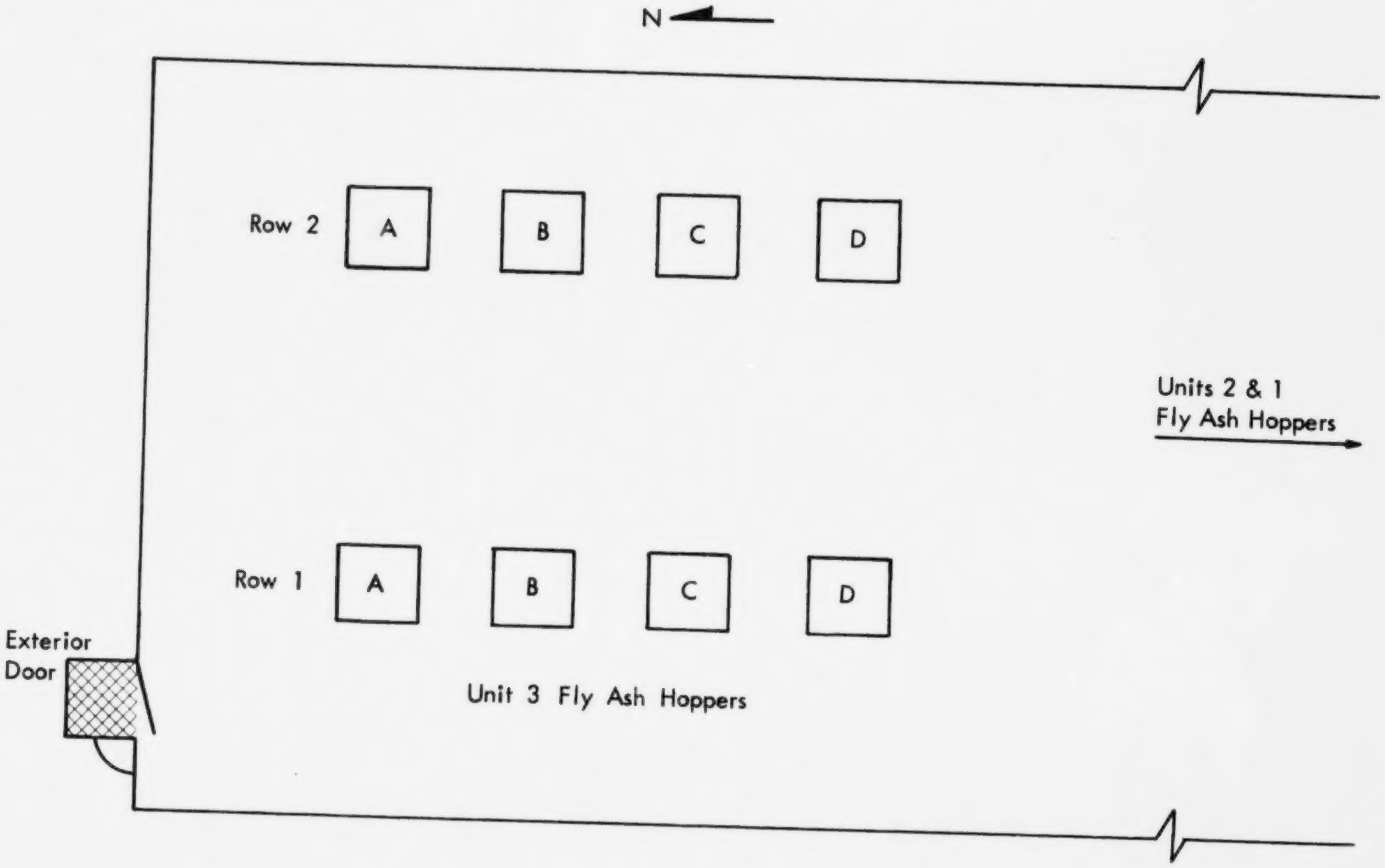

N
Row 2
A
B
C
D
Units 2 & 1
Fly Ash Hoppers
Row 1
A
B
C
D
Exterior
Door
Unit 3 Fly Ash Hoppers

Figure 13. ESP hopper arrangement, Plant No. 3.

Economizer Ash

Economizer ash was sampled directly from valves on the two collection hoppers for Unit No. 3. The economizers were located ahead of the ESP array. The economizer ash was sampled six times per day, and sampling was alternated between the two hoppers, as required by the RTI scheme.

Bottom Ash

The bottom ash accumulated in six collection hoppers. The ash was quenched and sluiced out once per shift. Dry ash was sampled by opening one of the six ports (6 in.) and withdrawing hot ash with a scoop on a 12- to 15-ft handle. The sampler was required to wear a full face shield. The plant operator in that area opened and closed the ports. RTI prepared a sampling schedule based on the configuration and wasting procedures for the bottom ash hoppers. Figure 14 shows a schematic representation of the bottom ash hopper system.

Coal

The plant personnel collected coal samples from the feed streams to each of the four pulverizers every 4 hr and prepared a daily composite.

Plant Background Air

Plant background air was sampled near the forced draft fans on the top floor of the plant building.

Continuous Monitoring

Ports similar to those on the outlet duct were located on both ducts inlet to the ESP. The inlet and outlet ports were on the same level with a walkway between the platforms (see Figures 10 and 11). The heated sampling line was dropped nearly vertically to the ground from the ports (130 ft) to the lab trailer.

SAMPLING LOCATIONS, PLANT NO. 4

Flue Gas Outlet

Eight ports were located on the top of the duct between the ESP and the stack breeching. The duct was 10 ft wide and 20 ft deep at this point. The ports were approximately 1 ft below removable deck grates. Figures 15 and 16 show top and side views of the duct and give approximate dimensions and distances to disturbances. Figure 17 is a cross sectional view of the flue gas outlet duct showing the location of the sample points within the duct. The outlet flue gas temperature was 320-350°F with a velocity of approximately 60 ft/sec. The flue gas was sampled until approximately 20 m^3 of flue gas was collected between two modified Method 5 sampling trains.

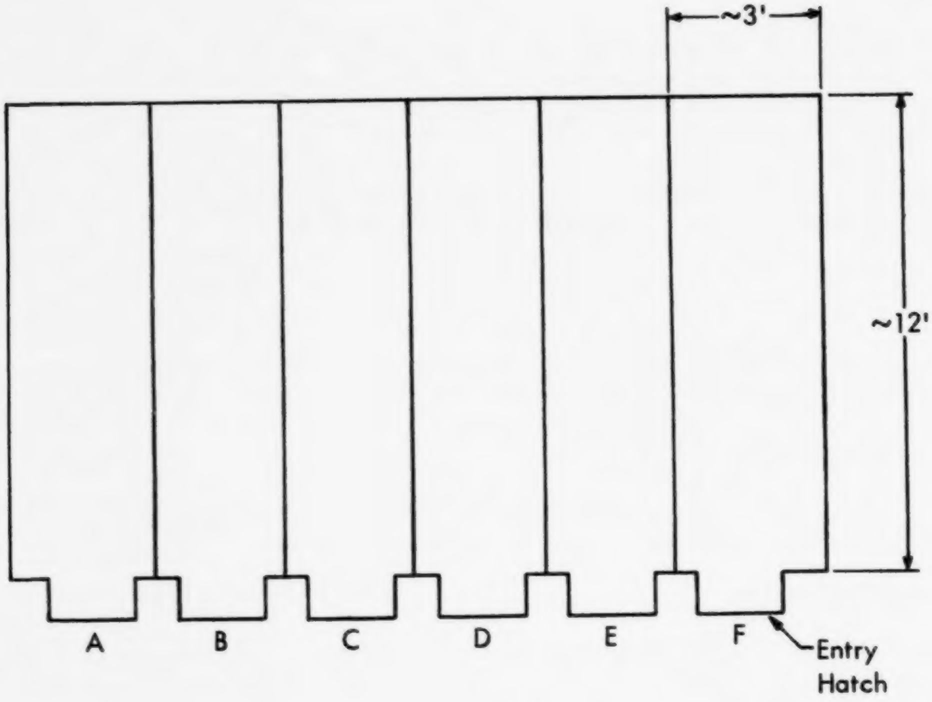
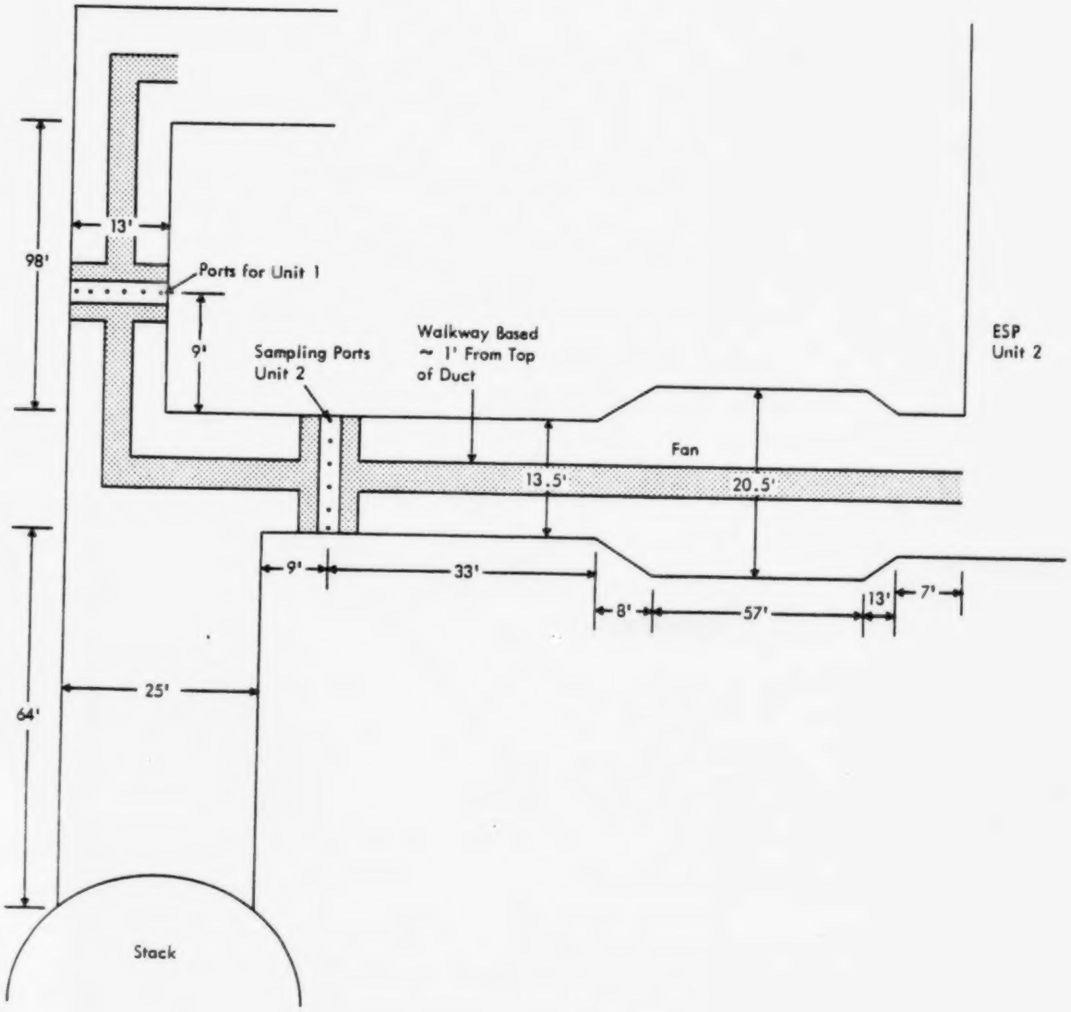

~3'
~12'
A
B
C
D
E
F
Entry Hatch

Figure 14. Schematic of the bottom ash hopper for Unit 3, Plant No. 3



13'
98'
Ports for Unit 1
9'
Sampling Ports
Unit 2
Walkway Based
~ 1' From Top
of Duct
ESP
Unit 2
Fan
13.5'
20.5'
9'
33'
8'
57'
13'
7'
25'
64'
Stack

Figure 15. Top view of the flue gas outlet duct and sampling points, Plant No. 4.

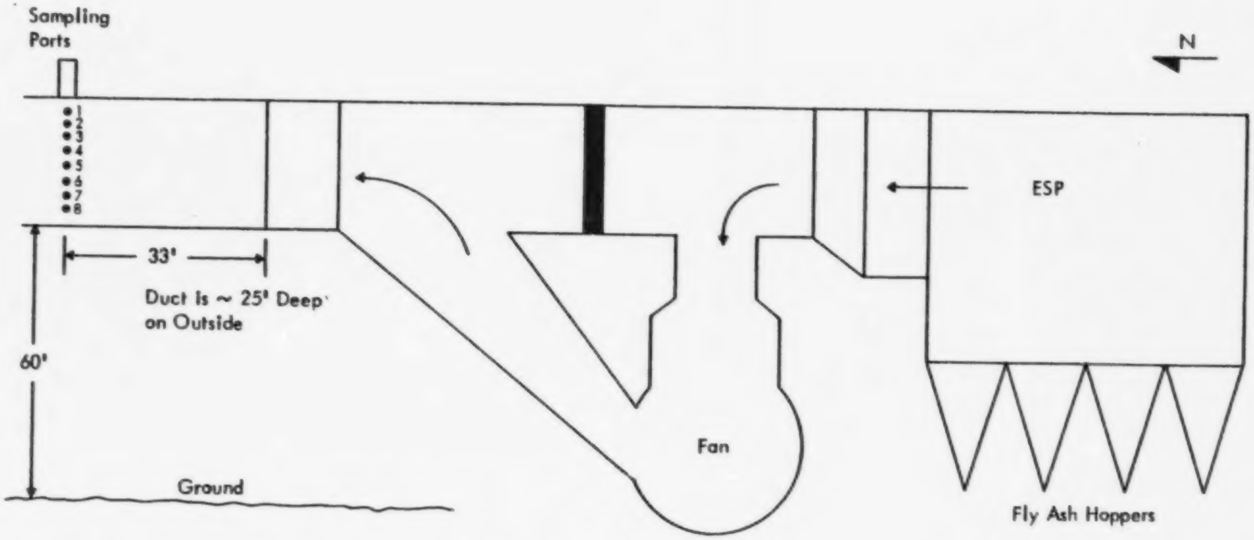
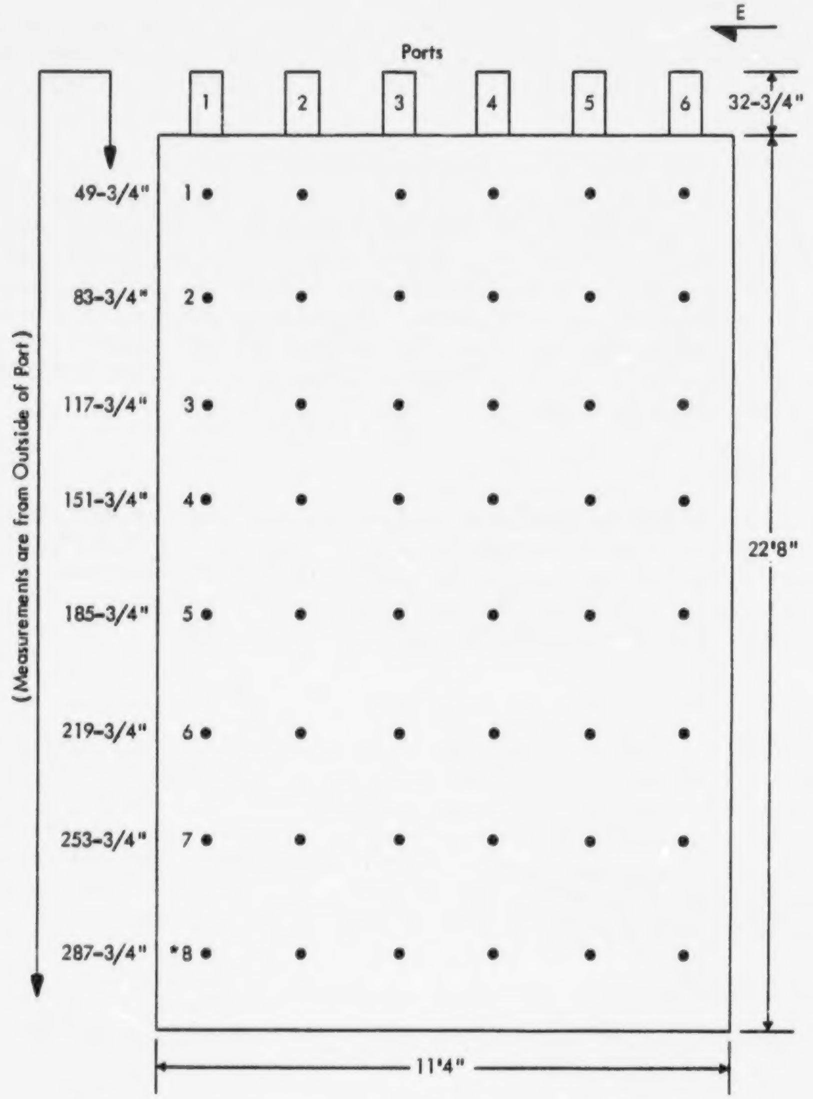

Sampling Ports
1
2
3
4
5
6
7
8
33'
Duct is ~ 25' Deep on Outside
60'
Ground
Fan
ESP
N
Fly Ash Hoppers

Figure 16. Side view of flue gas outlet duct and sampling points, Plant No. 4.


E
Ports
1
2
3
4
5
6
32-3/4"
(Measurements are from Outside of Port)
49-3/4"
83-3/4"
117-3/4"
151-3/4"
185-3/4"
219-3/4"
253-3/4"
287-3/4"
1
2
3
4
5
6
7
*8
22'8"
11'4"

* Point No. 8 was actually sampled at a point 282-3/4" inside the duct. This was due to a miscalculation in the design of the probe.

Figure 17. Cross-sectional view of the flue gas outlet duct showing the location of the sample points within the duct, Plant No. 4.

ESP Ash

The ESP hopper array consisted of five rows of four hoppers each. Figure 18 is an illustration of the ESP hopper array. Ash was removed from a port on the side of each hopper using a dipper. RTI constructed a hopper selection schedule to obtain a sample from each row six times per day.

Bottom Ash

Bottom ash was collected in four quench hoppers and was wasted once per shift. Ash was sluiced out of the hoppers, through a clinker grinder, out to the bottom ash pond approximately 2,000 ft from the plant building. Since the hoppers were not directly accessible for sample collection, samples were taken from the outlet pipe at the pond. Sampling personnel maintained close contact with the plant operators so that collection was conducted only when ash was sluiced from Unit No. 2. Three or four pint jars of ash-water slurry were taken three times per day.

Water

There was no effluent from the bottom ash wasting system other than the sluice water. Hence, the river water used to quench and sluice the ash was the only water sample to be collected. River water was used for the boiler seal with the overflow feeding the ash hopper. The raw river water was taken in duplicate from the screen intake house once per day.

Coal

The boilers were face-fired with pulverized coal. The coal was supplied via seven pulverizer mills. Samples were taken from the feed pipes above the mills according to a selection scheme provided by RTI. Three of the seven hoppers were not sampled due to obstructions and the inability to remove port caps. Figure 19 illustrates the feed pipe arrangement and indicates the six sampling points that were accessible. The plant burned primarily West Virginia coal with a fuel value of 12,000 Btu/lb and 11 to 12% ash.

Plant Background Air

Plant background air was sampled near the air intakes on the top floor of the plant building.

Continuous Monitoring

Ports for continuous monitoring were located on the duct between the boiler and the ESP.

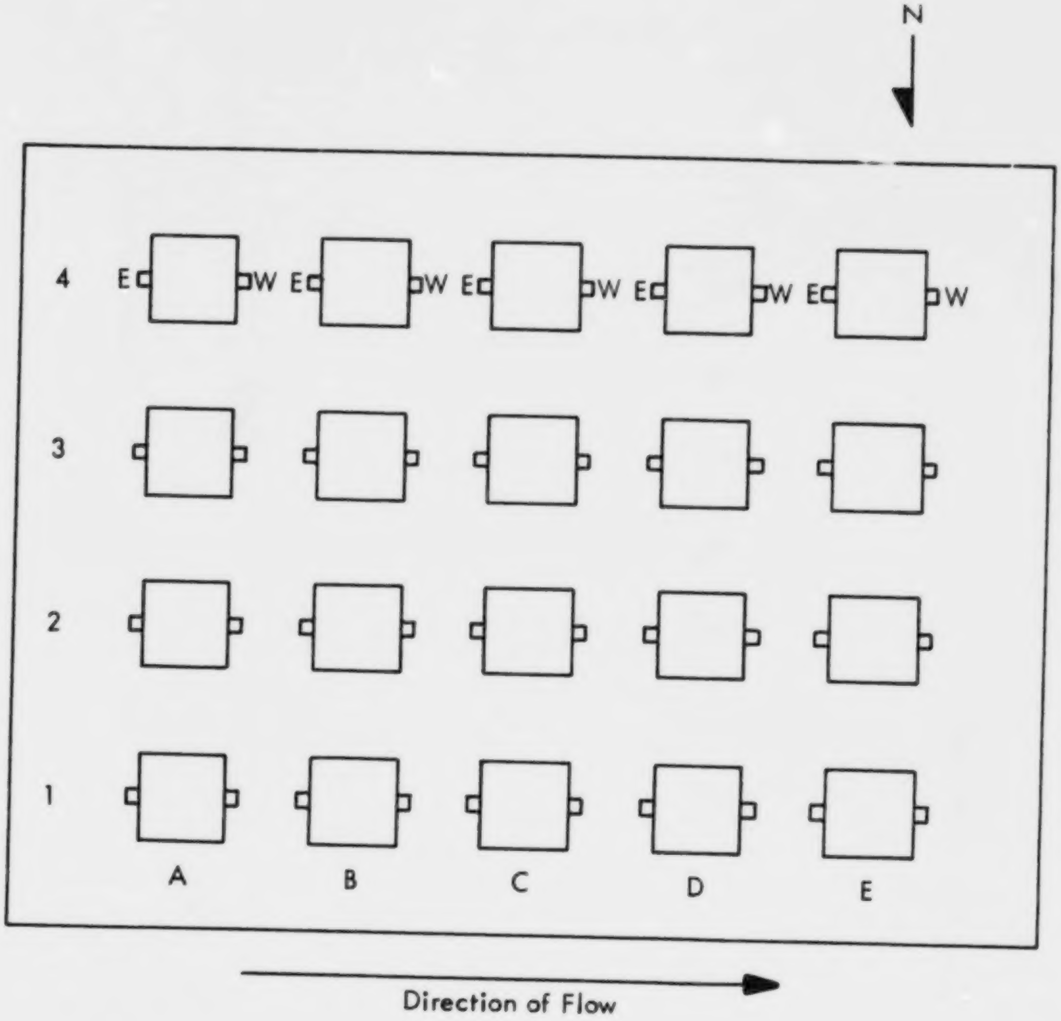

N
4
3
2
1
E
W
A
B
C
D
E
Direction of Flow

Figure 18. ESP hopper array, Plant No. 4.

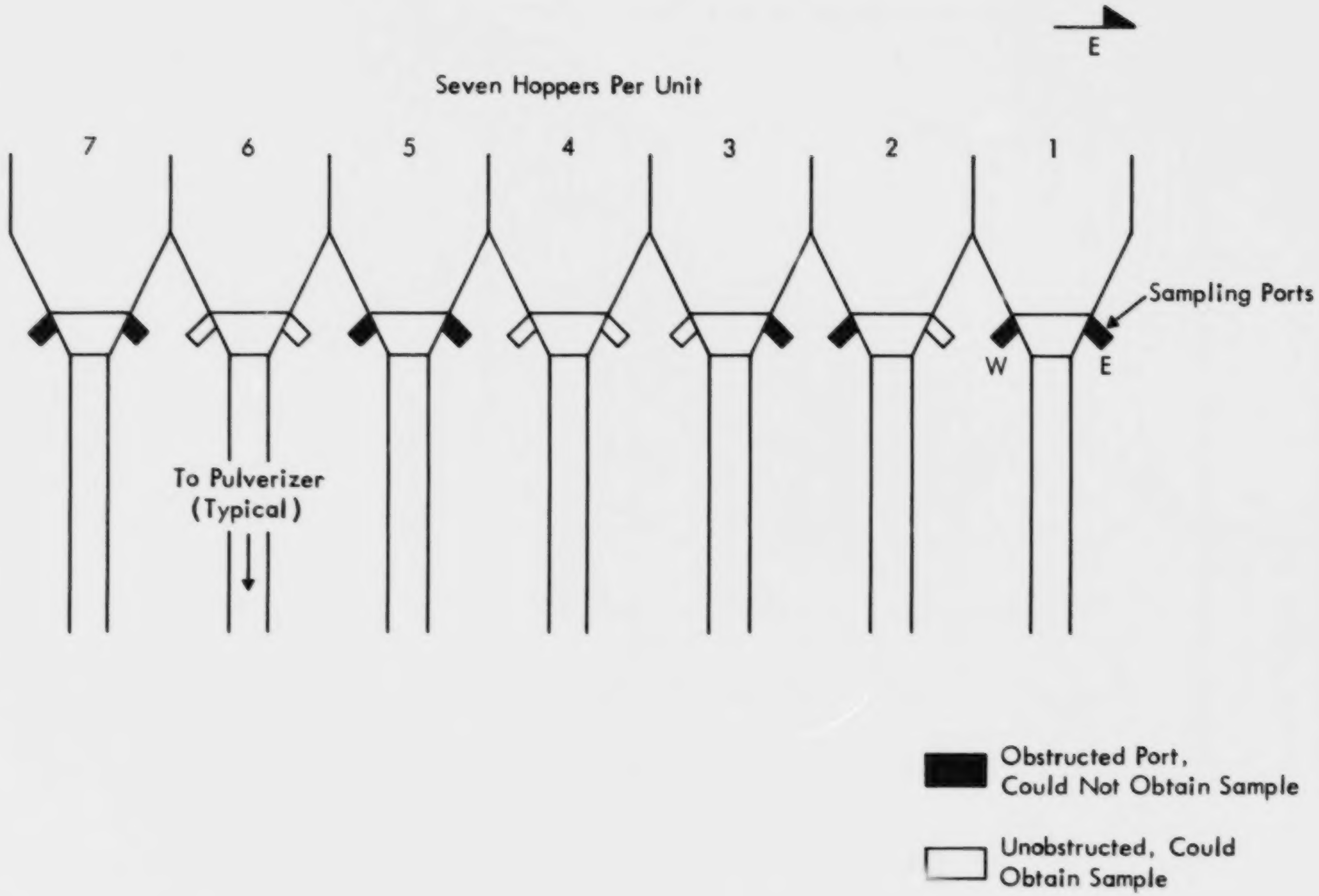

E
Seven Hoppers Per Unit
7
6
5
4
3
2
1
Sampling Ports
W
E
To Pulverizer
(Typical)
Obstructed Port,
Could Not Obtain Sample
Unobstructed, Could
Obtain Sample

Figure 19. Coal feeder arrangement, Plant No. 4.

SAMPLING LOCATIONS, PLANT NO. 5

The general layout of Plant No. 5 is shown in Figure 20.

Flue Gas Outlet

Four ports were located on the stack at the 96-ft level. The stack inner diameter was 21 ft at the sampling level. A vertical cross sectional view of the stack, shown in Figure 21, indicates elevations and distances to disturbances. Figure 22 is a horizontal cross sectional view of the stack at the sampling platform level showing the positions of the ports, the locations of the plant's continuous monitoring equipment, and the sampling traverse point locations. The distances of the traverse points from the inside stack wall are listed in Table 5.

ESP Ash

The two ESP units, shown in Figure 20, each consisted of three rows of four collection hoppers. The middle hoppers on each row of each ESP unit, labeled A1-3 and B1-3 on Figure 20, were fitted with valves for ash sampling. Samples were taken from all six of these hoppers six times per day.

Bottom Ash

Bottom ash was sluiced twice per shift from the three collection hoppers through two sluice lines per hopper into a common sump (see Figure 23). Bottom ash samples were taken using a long-handled dipper from the effluent of one of the sluice lines, i.e., at the sump, six times per day. The selection scheme for sampling ash from the three hoppers was provided by RTI. The sluiced ash was allowed to settle in a bucket for 30 min and the supernatant decanted prior to transferring the sample to a jar for storage and shipment. A portion of the supernatant was transferred to a water bottle as the corresponding quench water effluent sample.

Water

Quench water effluent samples were taken six times per day as described above. Quench water influent samples were taken once per day from a tap on the quench water supply line near the bottom ash hoppers.

Coal

Coal samples were taken six times per day from one of the feed streams to the five pulverizer mills. The sampling locations and stream identification system are shown in Figure 24. The feed stream selection scheme was provided by RTI.

Plant Background Air

Plant background air was sampled from the forced draft fan room on the ground floor of the plant building.

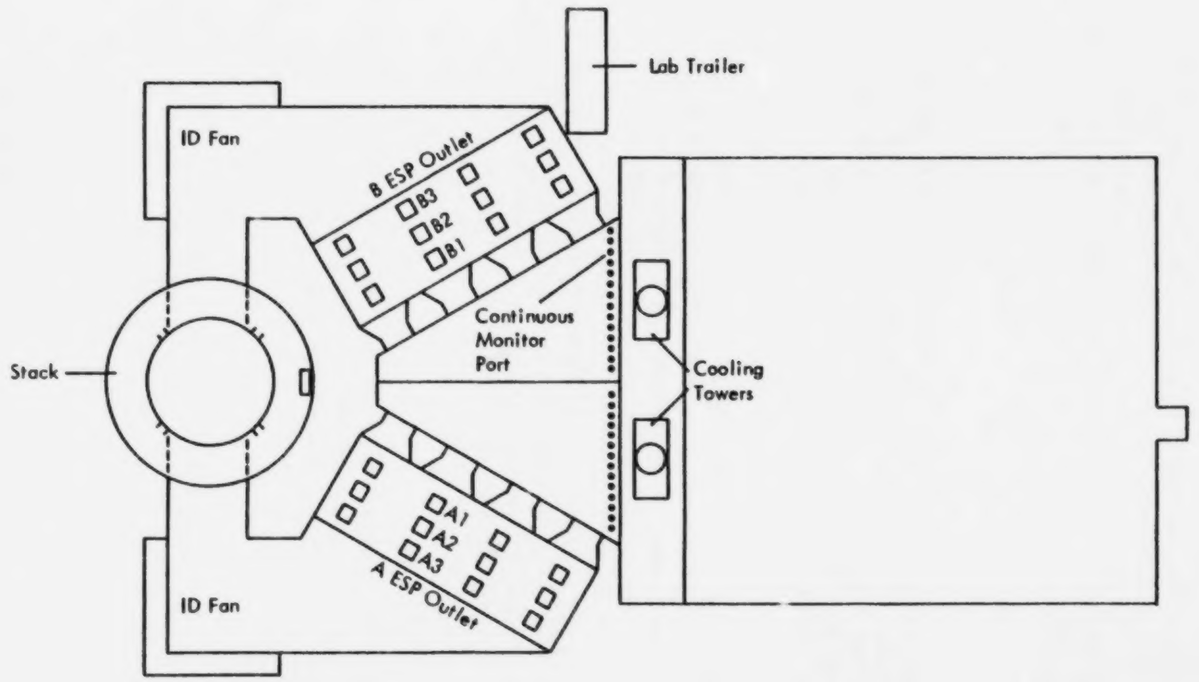

Lab Trailer
ID Fan
B ESP Outlet
B3
B2
B1
Continuous
Monitor
Port
Stack
Cooling
Towers
A1
A2
A3
A ESP Outlet
ID Fan

Figure 20. General layout of Plant No. 5

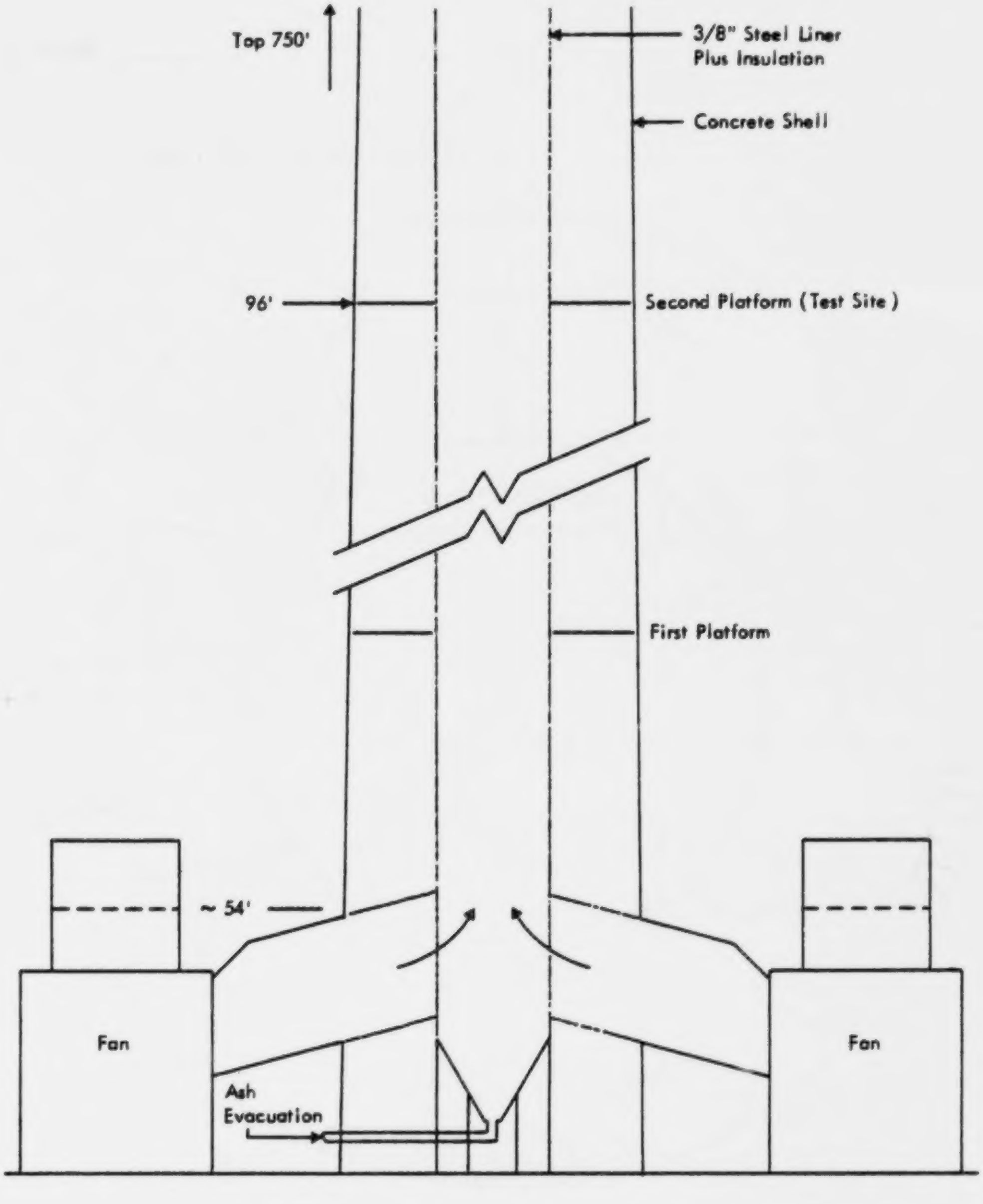

Top 750'
3/8" Steel Liner Plus Insulation
Concrete Shell
96'
Second Platform (Test Site)
First Platform
~ 54'
Fan
Fan
Ash Evacuation

Figure 21. Vertical cross section of stack, Plant No. 5.

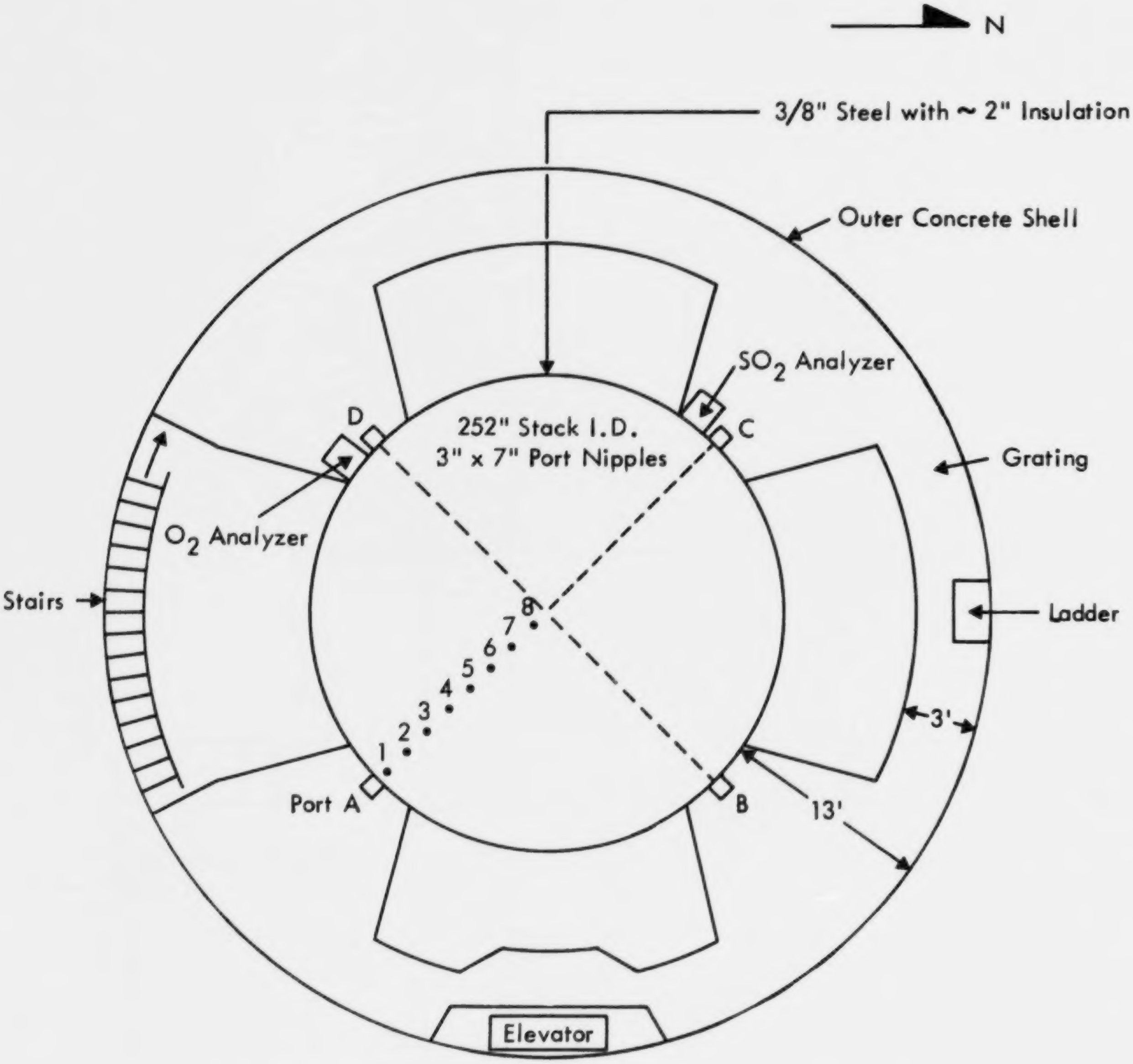

N
3/8" Steel with ~ 2" Insulation
Outer Concrete Shell
SO_2 Analyzer
252" Stack I.D.
3" x 7" Port Nipples
D
C
Grating
O_2 Analyzer
Stairs
Ladder
8
7
6
5
4
3
2
1
3'
Port A
B
13'
Elevator

Figure 22. Horizontal stack cross section and traverse point locations, Plant No. 5.

TABLE 5. MODIFIED METHOD 5 TRAIN SAMPLE POINT LOCATIONS, PLANT NO. 5

Traverse point no.	Fraction of stack ID (%)	Distance from inside wall (in.)
1	1.6	4.0
2	4.9	12.4
3	8.5	21.4
4	12.5	31.5
5	16.9	42.6
6	22.0	55.4
7	28.3	71.3
8	37.5	94.5

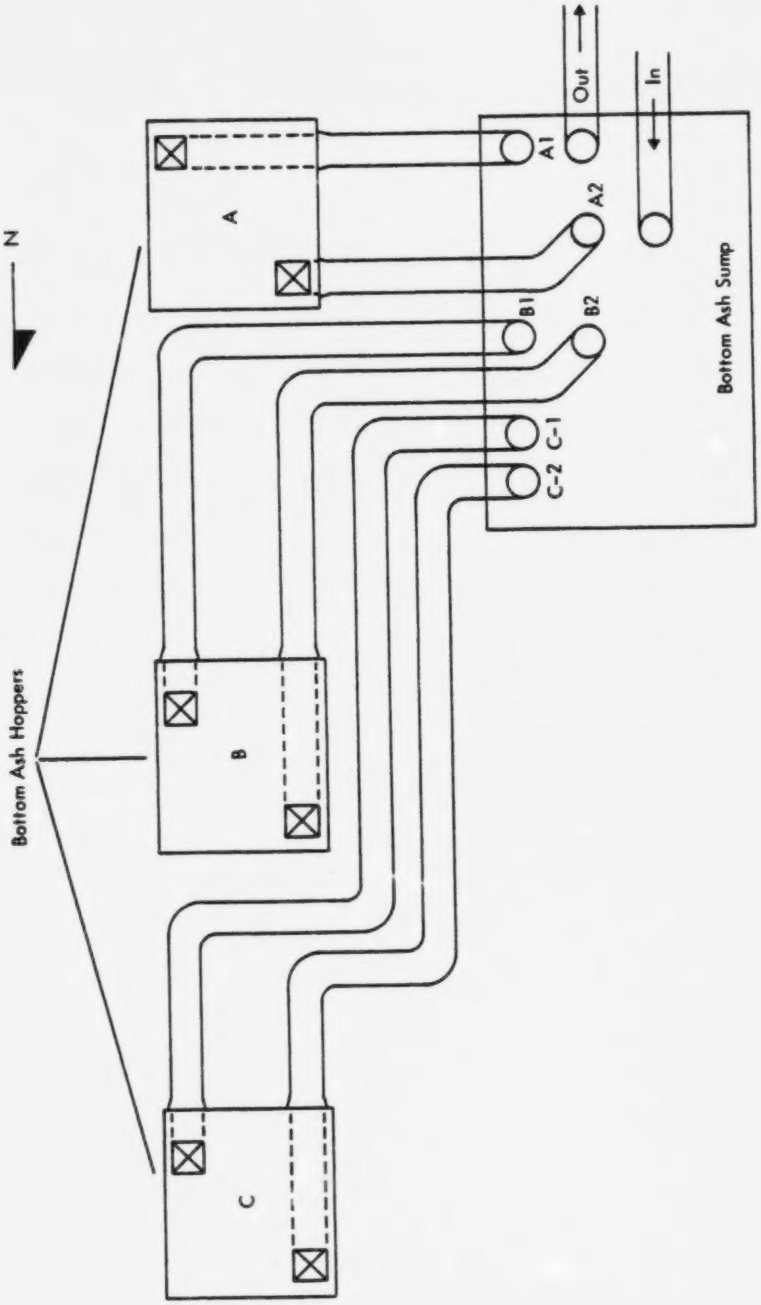

Bottom Ash Hoppers
N
A
B
C
A1
A2
B1
B2
C-1
C-2
Out
In
Bottom Ash Sump

Figure 23. Bottom ash sluice system, Plant No. 5.

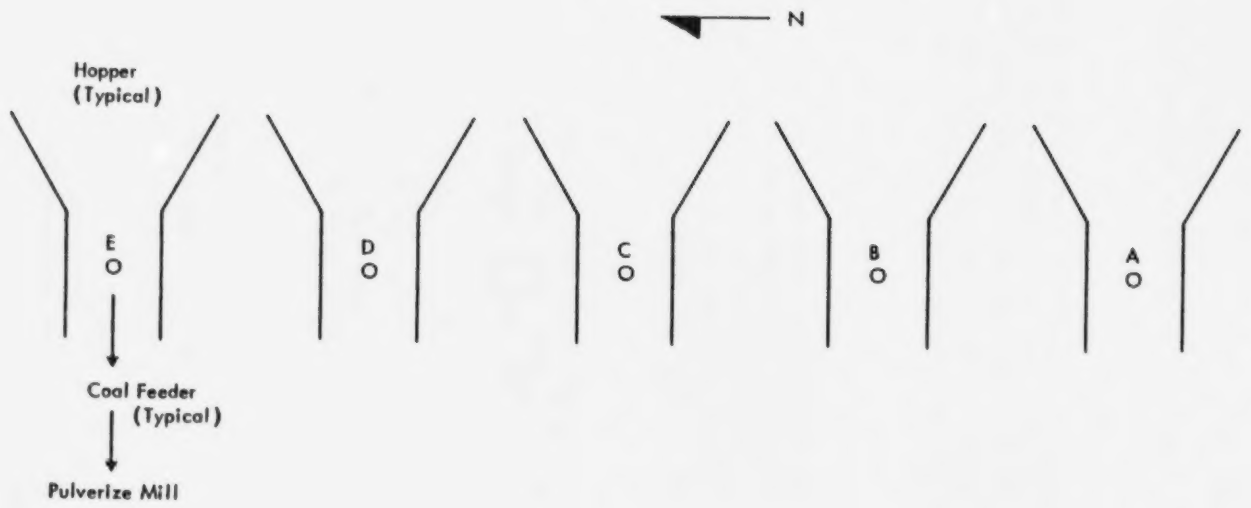

N
Hopper
(Typical)
E
D
C
B
A
Coal Feeder
(Typical)
Pulverize Mill

Figure 24. Coal sampling locations, Plant No. 5.

Continuous Monitoring

Ports for continuous monitoring were located on the ducts between the boiler and the two ESP units. A port on the B side duct was sampled (see Figure 20).

SAMPLING LOCATIONS, PLANT NO. 6

The general layout of Plant No. 6 is shown in Figure 25.

Flue Gas Outlet

Eight ports were located in a vertical row 4 ft upstream from the stack. The location of the ports is shown in the verical cross sectional view in Figure 26 and the horizontal view in Figure 27. The very close proximity of the ports to flow disturbances necessitated use of the maximum number of traverse points. The duct dimensions and locations of the 48 traverse points are shown in Figure 28.

ESP Ash

The ESP array, shown in Figure 27, consisted of two rows of four hoppers. Ash samples were taken 6 times per day from ports on one hopper from each row according to a selection scheme provided by RTI. Since samples could not be taken from hoppers 1A and 2A because the ports were obstructed, alternate hoppers in row A were selected by RTI for these two points.

Bottom Ash

Bottom ash samples were taken six times per day from the sluice line effluent at the ash pond. Samples were collected, allowed to settle, and decanted prior to transferring to the sample container.

Waters

Quench water effluent was taken from the bottom ash sample decantate six times per day. Quench water influent was sampled once per day from a tap on the supply line to the bottom ash quench system.

Coal

Coal samples were collected six times per day from one of the four hoppers located above the pulverizer mills. The sampling locations are identified in Figure 29.

Plant Background Air

Plant background air was sampled near the forced draft fans located directly beneath the ESP unit.

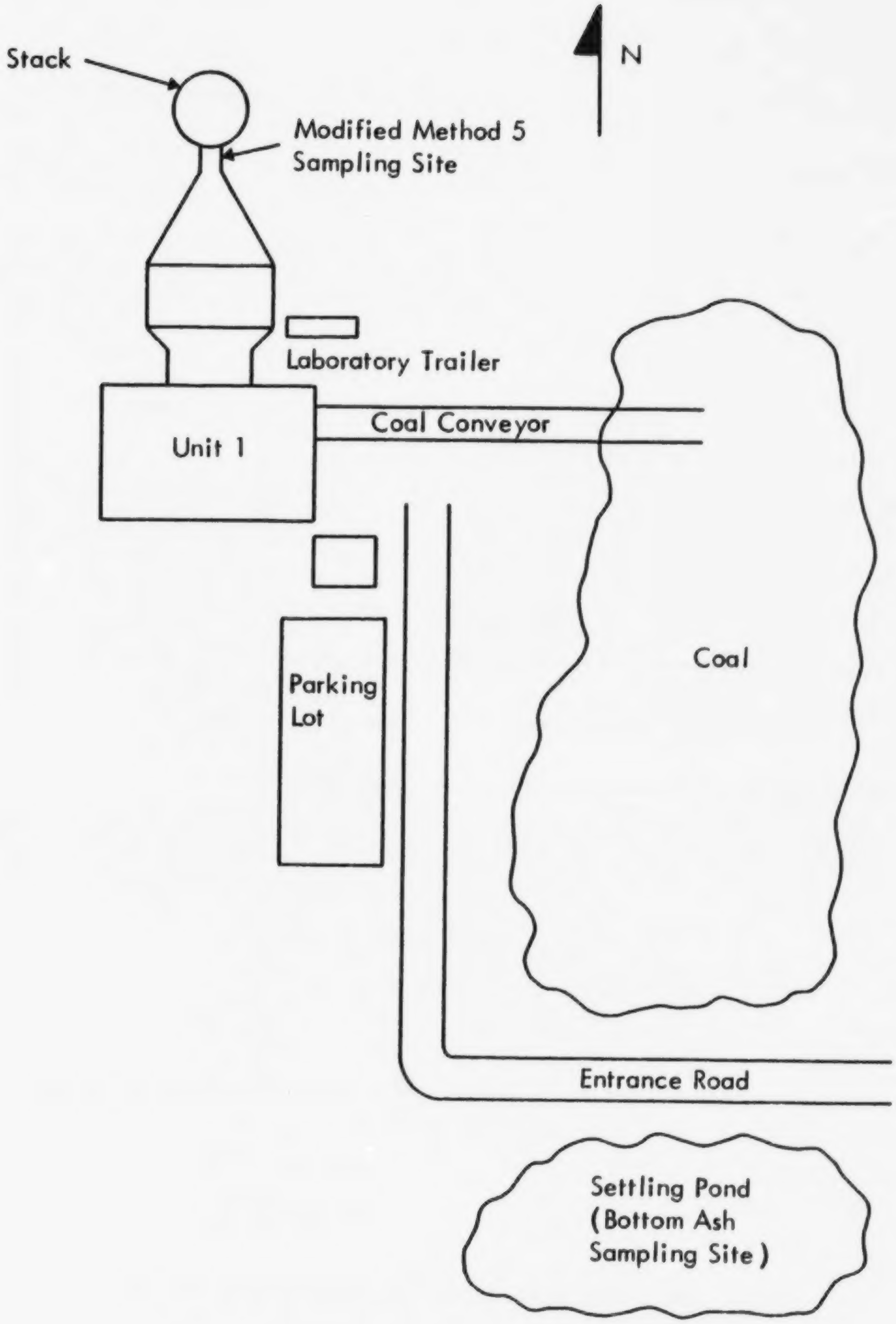

Stack
N
Modified Method 5
Sampling Site
Laboratory Trailer
Coal Conveyor
Unit 1
Parking
Lot
Coal
Entrance Road
Settling Pond
(Bottom Ash
Sampling Site)

Figure 25. General layout of Plant No. 6.

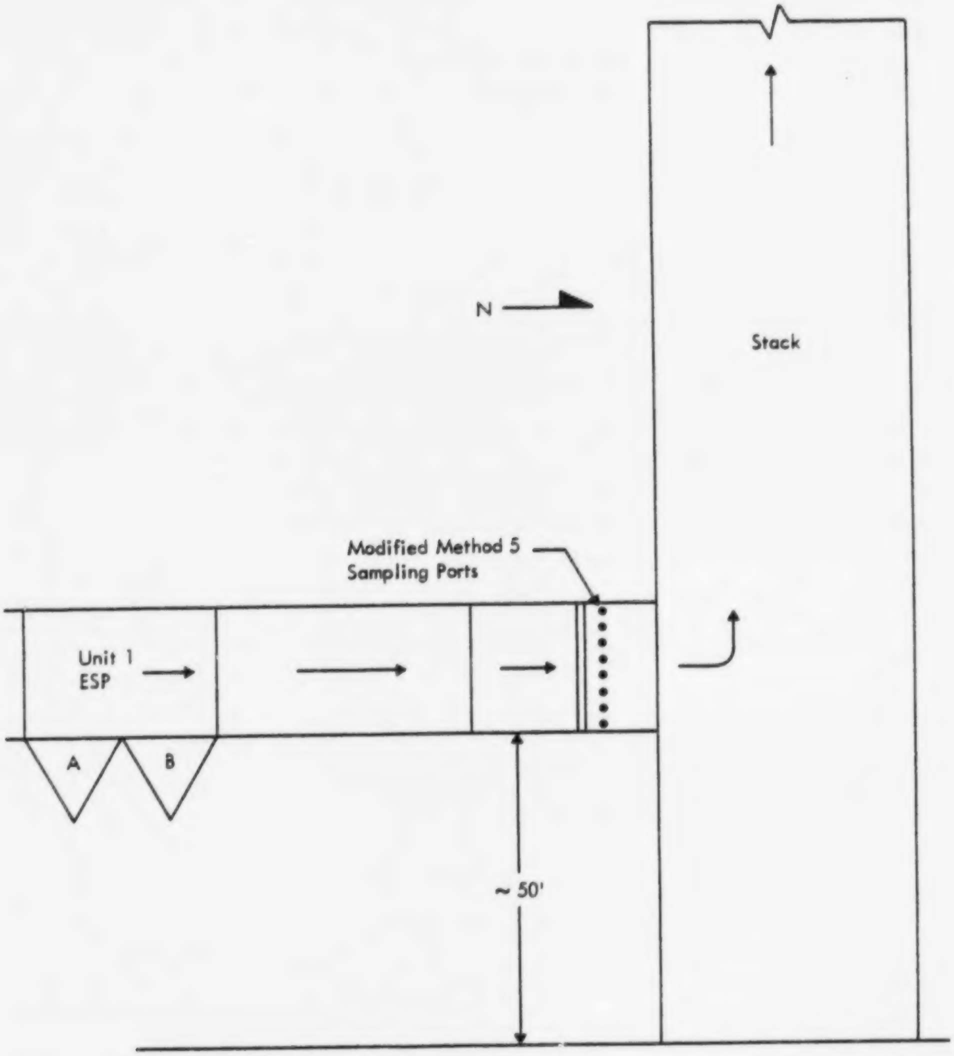

Stack
N
Modified Method 5
Sampling Ports
Unit 1
ESP
A
B
~ 50'

Figure 26. Vertical cross section, Plant No. 6.

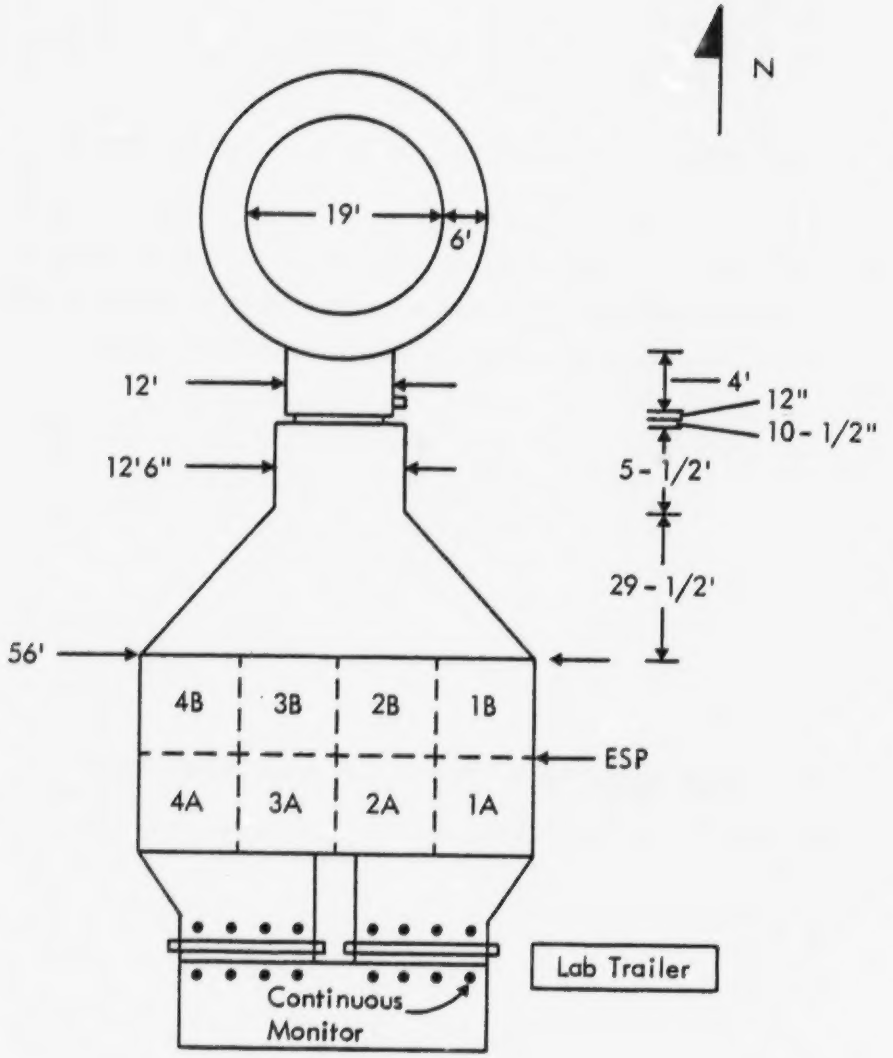

N
19'
6'
12'
12'6"
56'
4'
12"
10- 1/2"
5 - 1/2'
29 - 1/2'
4B
3B
2B
1B
ESP
4A
3A
2A
1A
Lab Trailer
Continuous Monitor

Figure 27. Horizontal view, Plant No. 6.

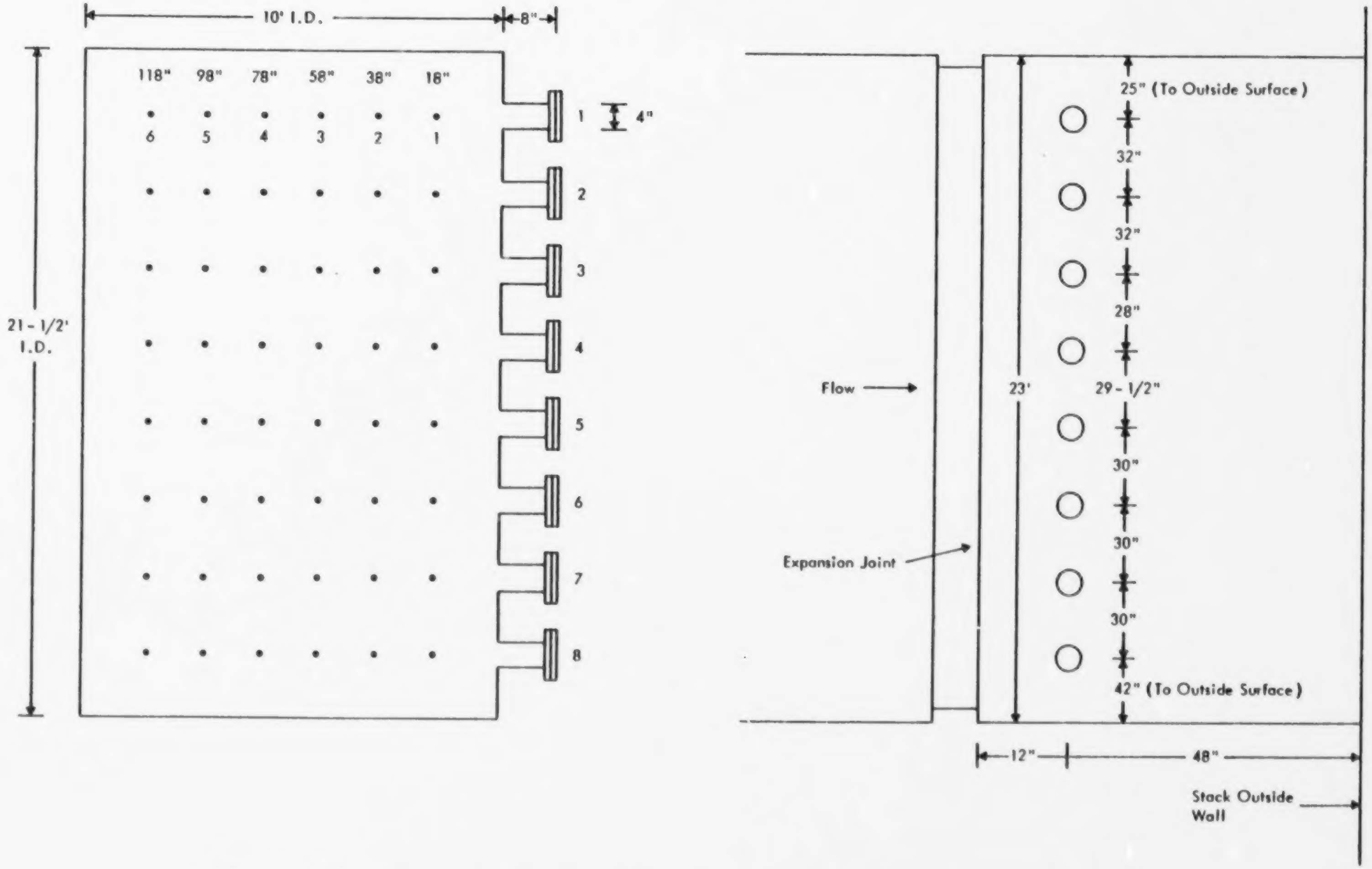

10' I.D.
8"
21 - 1/2' I.D.
118"
98"
78"
58"
38"
18"
6
5
4
3
2
1
1
2
3
4
5
6
7
8
4"
Flow
Expansion Joint
23'
25" (To Outside Surface)
32"
32"
28"
29 - 1/2"
30"
30"
30"
42" (To Outside Surface)
12"
48"
Stack Outside Wall

Figure 28. Duct dimensions and traverse point locations, Plant No. 6.

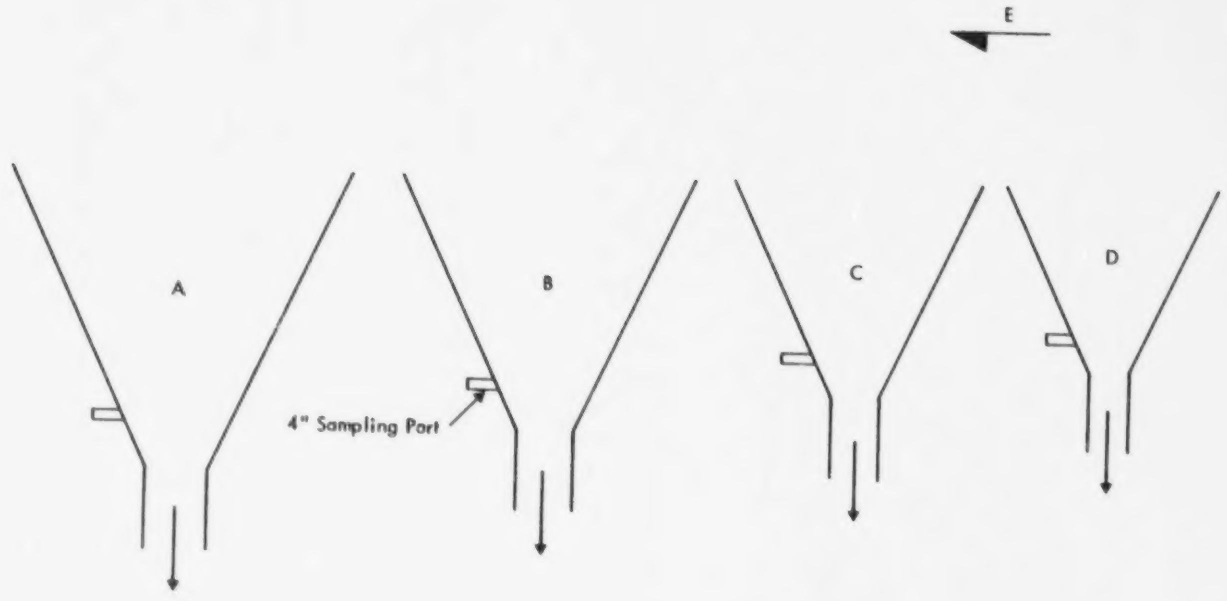

E
A
B
C
D
4" Sampling Port

Figure 29. Coal sampling locations, Plant No. 6.

Continuous Monitoring

Ports for continuous monitoring were located on the duct immediately upstream from the ESP unit (see Figure 27).

SAMPLING LOCATIONS, PLANT NO. 7

The general layout for Plant No. 7 is shown in Figure 30.

Flue Gas Outlet

Ten ports were located on each of two ducts entering opposite side of the stacks (see Figure 30). The ports were accessed by four platforms on each duct. As in the case of Plant No. 6, the proximity of the ports to disturbances necessitated use of a large number of traverse points (50 points on each duct). Figure 31 shows the locations of traverse points on a cross section of the side B duct. The side A duct differed only in the position of the platforms relative to the duct.

ESP Ash

The two ESP units consisted of arrays of three rows of eight hoppers. Samples were taken from the pneumatic waste lines of both units six times per day. The ESP arrays and ash sampling points are shown in Figure 30.

Bottom Ash

Bottom ash was sluiced from the boiler once each operations shift. Samples of the sluiced ash were collected from the sluice line effluent at the ash pond three time per day. Samples were allowed to settle and were decanted prior to transferring to the sample container.

Economizer Ash

Economizer ash was sampled six time per day from one of the five hoppers. The locations and identifications of the hoppers are shown in Figure 30. The hoppers were selected according to a scheme provided by RTI.

Waters

Quench water effluent was taken from the bottom ash sample decantate three time per day. Quench water influent was sampled three times per day from a tap on the quench water supply line near the main pump.

Coal

Coal samples were taken six times per day from one of six feed streams to the pulverizer mills. The stream selection scheme was provided by RTI.

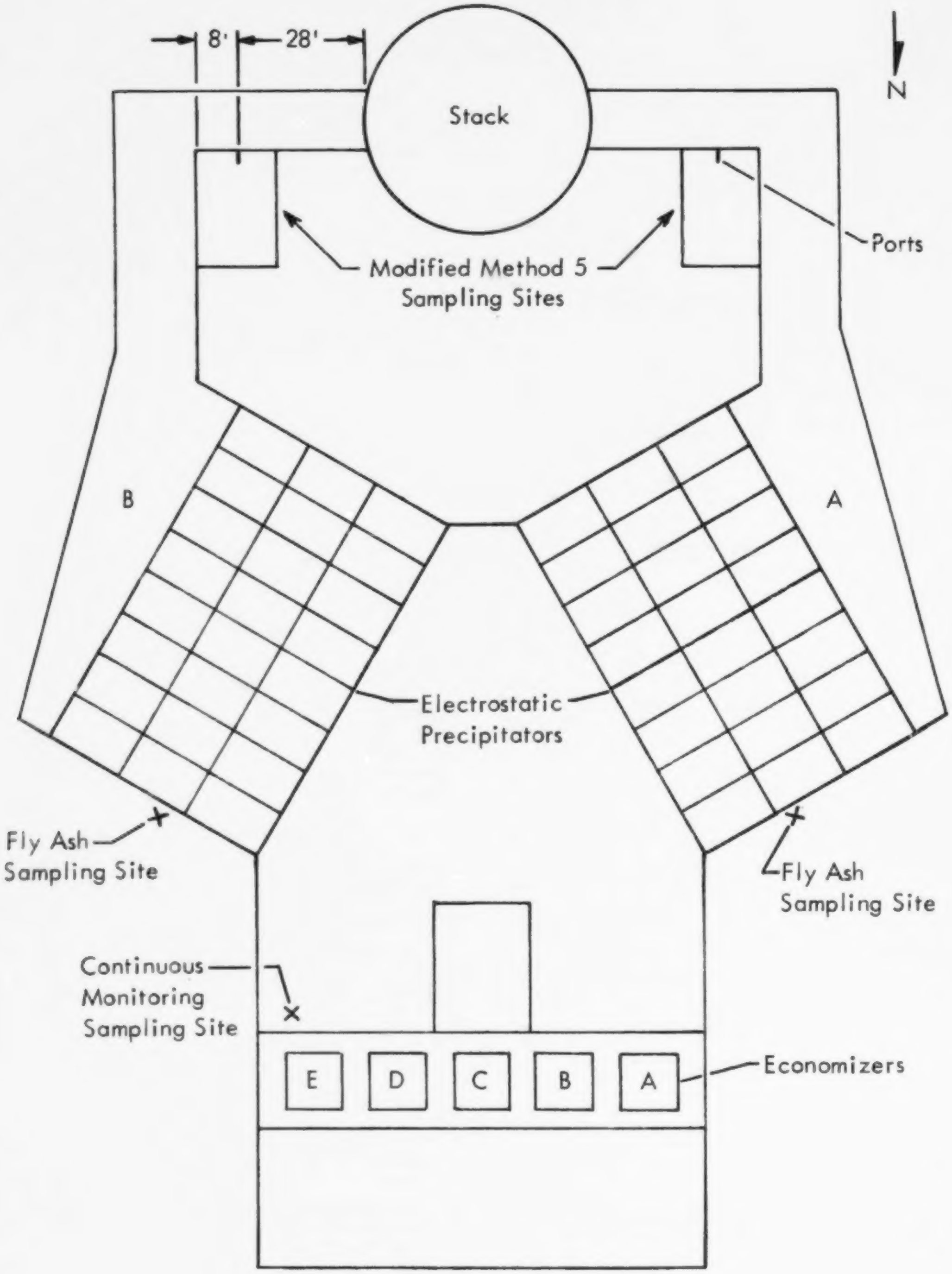

8'
28'
Stack
N
Ports
Modified Method 5
Sampling Sites
B
A
Electrostatic
Precipitators
Fly Ash
Sampling Site
Fly Ash
Sampling Site
Continuous
Monitoring
Sampling Site
E
D
C
B
A
Economizers

Figure 30. General layout of Plant No. 7.

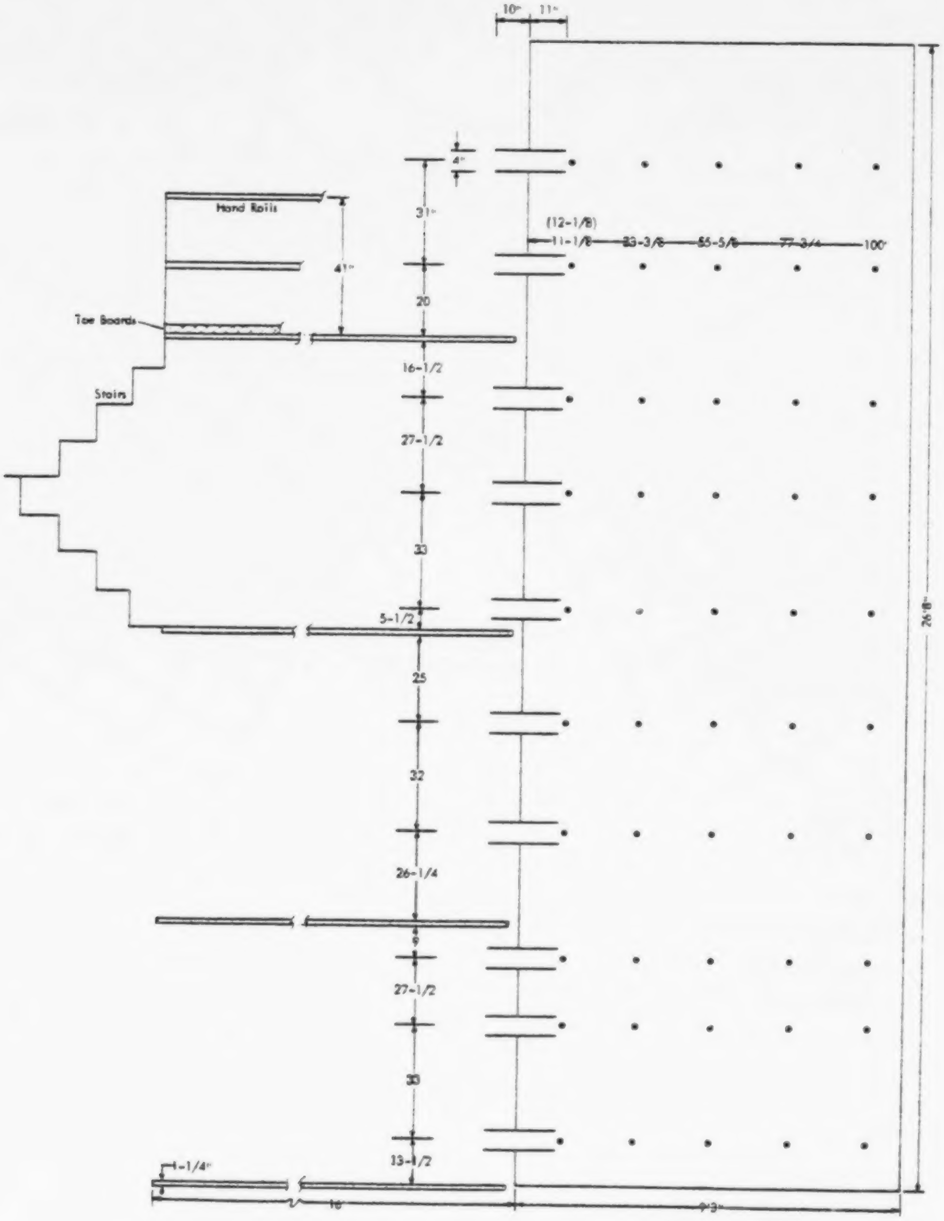

10"
11"
4"
Hand Rails
31"
41"
(12-1/8)
11-1/8
33-3/8
55-5/8
77-3/4
100"
Toe Boards
20
16-1/2
Stairs
27-1/2
33
5-1/2
25
32
26-1/4
9
27-1/2
33
13-1/2
1-1/4"
16'
9'3"
26'8"

Figure 31. Duct dimensions and traverse point locations, side B, Plant No. 7.

Plant Background Air

Plant background air was sampled near the forced draft fans located under the main ducts between the plant building and the ESP units.

Continuous Monitoring

Ports for continuous monitoring were located on the duct immediately adjacent to the plant building and upstream of the ESP units. The location of the port used is noted on Figure 30.

SECTION 6

ANALYSIS METHODS

The general procedures for the preparation and analysis of samples from the power plants are described in the methods manual in Appendix A. This section provides descriptions of specific procedures used for sample compositing (e.g., solid and aqueous grab samples), extract compositing, and extract cleanup as well as other details related to the analyses of samples from the four plants.

GENERAL ANALYTICAL SCHEME

Sample preparation and analysis followed the general analytical scheme presented in Figure 32. The samples were spiked with surrogate compounds just prior to extraction. A representative fraction of the extracts for each sample type from Plants Nos. 1-4 was screened by fused silica capillary gas chromatography using Hall and flame ionization detectors (HRGC/Hall-FID) to provide preliminary information on the presence of chlorinated compounds. The extracts were then analyzed by fused silica capillary gas chromatography/mass spectrometry (HRGC/MS) to provide information on the recovery of surrogate compounds and quantitation of polynuclear aromatic hydrocarbons, phthalates, and other major components of the sample extracts. The extracts were combined as necessary to provide 5-day composites for HRGC/MS-SIM (selected ion monitoring) analyses of PCBs, PCDDs and PCDFs. If any tentative identifications of PCDDs or PCDFs were made by HRGC/MS-SIM, HRGC with high resolution mass spectrometry (HRGC/HRMS-SIM) was used to confirm the identification and to quantitate.

SAMPLE COMPOSITING AND EXTRACTION

Ash, coal, and aqueous samples (excluding water samples collected once per day or less) were combined to form daily composite samples prior to analysis. These composites were prepared by combining equal weights for the samples (usually six) collected during that 24-hr period. Since compounds of interest were not identified in grab samples from the first three plants, the daily composites prepared for Plants Nos. 4-7 were further combined into 5-day composites prior to extraction. Hence, the number of extracts for subsequent analysis was decreased.

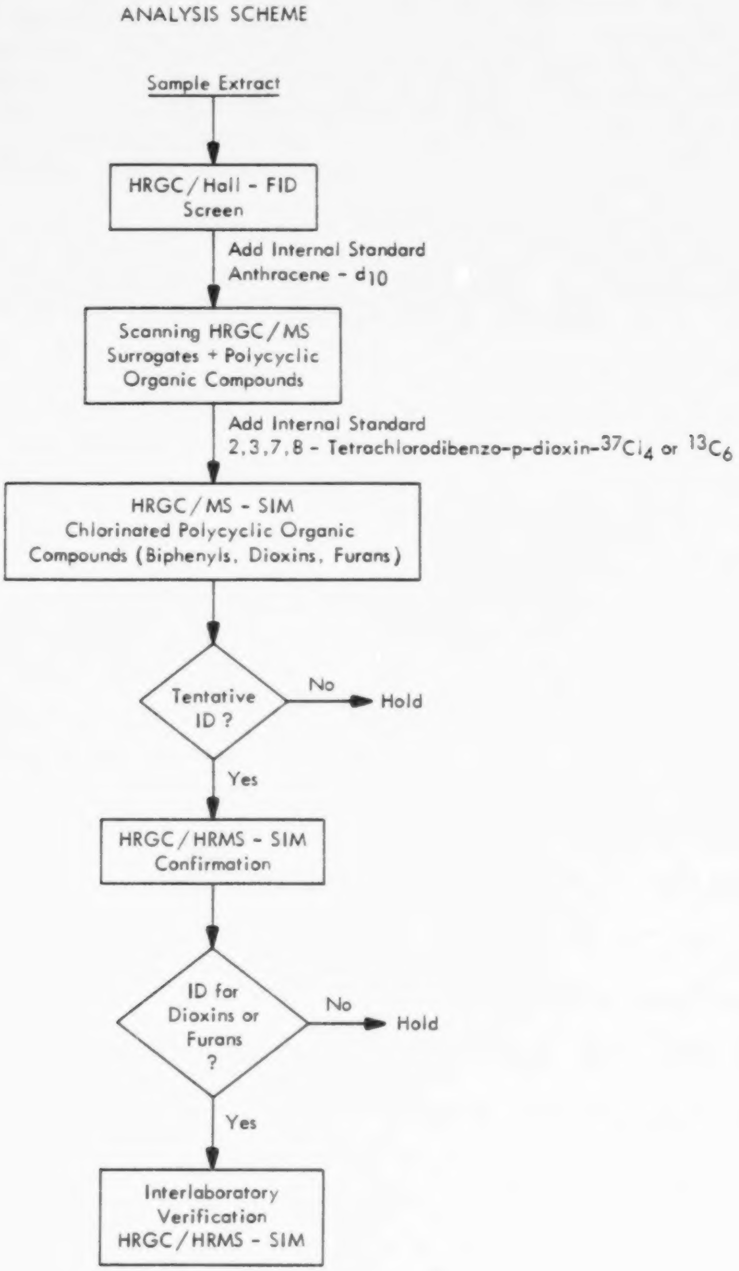

ANALYSIS SCHEME
Sample Extract
HRGC/Hall - FID Screen
Add Internal Standard Anthracene - d_{10}
Scanning HRGC/MS Surrogates + Polycyclic Organic Compounds
Add Internal Standard 2,3,7,8 - Tetrachlorodibenzo-p-dioxin-$^{37}Cl_4$ or $^{13}C_6$
HRGC/MS - SIM Chlorinated Polycyclic Organic Compounds (Biphenyls, Dioxins, Furans)
Tentative ID ?
No
Hold
Yes
HRGC/HRMS - SIM Confirmation
ID for Dioxins or Furans ?
No
Hold
Yes
Interlaboratory Verification HRGC/HRMS - SIM

Figure 32. Analysis scheme for sample extracts.

The ESP ash samples for Plants Nos. 2-6 were collected from multiple hoppers for each time period. The ESP ash samples for each collection time were composited to form a representative ash for each collection time. The daily composites were prepared from the time period composites as described in the preceding paragraph. The compositing schemes were developed from the estimated fractions of total ESP ash collected in each row of hoppers as provided by the plant management. The estimated fractions of the total ESP ash collected in each row of hoppers at Plants Nos. 2-6 are shown in Table 6. The composite samples for each collection time were prepared by mixing weights of the samples from each hopper row proportional to the fraction of ash collected in the row.

TABLE 6. ESTIMATED PERCENT FLY ASH COLLECTED IN EACH ROW OF ESP HOPPERS, PLANTS NOS. 2-6[a]

Plant No.	Row 1	Row 2	Row 3	Row 4	Row 5
2[b]	75	19	5	1	-
3[c]	95	5	-	-	-
4[d]	75	19	5	1	< 1
5[e]	85	13	2	-	-
6[f]	75	19	-	-	-

[a] Data provided by plant managements.

[b] Four rows of ESPs with eight hoppers each.

[c] Two rows of ESPs with four hoppers each.

[d] Five rows of ESPs with eight hoppers each.

[e] Two ESPs with three rows of four hoppers on each unit.

[f] Two rows with four hoppers each.

Immediately prior to extraction, all composite and other grab samples prepared for extraction were spiked with 50 µg of each of the surrogate spiking compounds. These were naphthalene-d_8, chrysene-d_{12}, 1,2,4,5-tetrachlorobenzene-$^{13}C_6$, pentachlorophenol-$^{13}C_6$, and 3,4,3',4'-tetrachlorobiphenyl-d_4. All daily grab composites from Plants Nos. 1, 2, and 3 and the 5-day grab composites from Plants Nos. 4-7 were analyzed in duplicate as described in Appendix A.

The surrogate spiking compounds were selected from commercially available stable labeled compounds to represent specific classes of the target analytes. Naphthalene-d_8 and chrysene-d_{12} were selected to represent small and large PAH compounds. Naphthalene is the most volatile of the target analytes. Hence, naphthalene-d_8 recoveries may provide an indication of maximum losses attributable to volatilization during extraction and extract concentration. Chrysene-d_{12} is the least volatile of the surrogate compounds. Chlorinated benzenes and biphenyls were represented by 1,2,4,5-tetrachlorobenzene-$^{13}C_6$ and 3,4,3',4'-tetrachlorobiphenyl-d_4. Pentachlorophenol-$^{13}C_6$ was selected to represent the most polar of chlorinated phenols.

The flue gas samples consisted of the cyclone catch, filter, adsorbent resin, and probe rinse. Each media was extracted separately and the extracts were combined to prepare a composite flue gas sample. Two modified method 5 sampling trains were used to collect 20 m^3 of flue gas for each day. Hence, the two composite flue gas samples were combined to make a daily composite unless there was some question as to the validity of the sampling procedure for a particular sampling train. The surrogate compounds (50 µg each) were added to different train components for different sampling days as a means to check the recovery efficiencies of individual components. The surrogate compounds were spiked in the adsorbent resin for sampling days 1 and 4, the train rinses for days 2 and 5, and the filter for day 3 for each plant. The first impinger contents for each of the sampling trains were extracted but the extract was not combined with the flue gas sample extracts. This sample was used to test for breakthrough of analytes from the resin.

Field sample blanks and laboratory method blanks were prepared and extracted as described in Appendix A.

HRGC/HALL-FID SCREEN

A representative fraction of the extracts for each sample type from Plants Nos. 1-4 were screened by HRGC/Hall-FID to determine if chlorinated compounds were present in the samples prior to HRGC/MS analyses. The analyses were completed using the instrument and parameters designated in Table 7. Although extract screening provided useful information on the compositions of samples from the first four plants, the results did not justify the labor expended. Hence, screening was discontinued for samples from Plant Nos. 5 to 7.

TABLE 7. INSTRUMENT AND OPERATING PARAMETERS FOR HRGC/HALL-FID SCREENING

Instrument	Tracor 550
Detectors	Model 700A Hall electrolytic conductivity (halogen mode) and hydrogen flame ionization 1:1 split
Column	15 m fused silica, wall-coated with DB-5
Column temperature	60° - 325°C at 8°C/min
Carrier gas	helium at 18 psi
Injector	J & W on-column (1 μl injection)

The column performance and Hall detector sensitivity were evaluated at least once per week using a performance standard developed for this study. The standard contained 11 halogenated compounds representing nonpolar, acidic, and basic classes. Figure 33 is a representative chromatogram of the column performance standard mixture. This mixture provided information regarding separation efficiency, adsorption of specific classes of compounds and pH of the column. The five-component surrogate compound mixture was also run at least twice per day to check the sensitivity of the flame ionization and Hall electrolytic conductivity detectors.

SCANNING HRGC/MS

The sample extracts were analyzed by scanning HRGC/MS to identify and quantitate polynuclear aromatic hydrocarbons (PAH), phthalates, and any chlorinated compounds that might be present. Table 8 lists the target PAH and phthalate compounds. The gas chromatography parameters for the separation of the sample extracts were essentially the same as that used for HRGC/Hall-FID screening. The gas chromatography and mass spectrometer instrumental parameters for the scanning HRGC/MS analyses are given in Table 9. Anthracene-d_{10} (20 μg) was added to sample extracts and standards prior to scanning HRGC/MS to serve as an internal standard for quantitation. The five-component surrogate compound standard (25 ng/μl each) and a 20 or 25 ng/μl PAH-phthalate standard were analyzed at least once per day with the sample extracts.

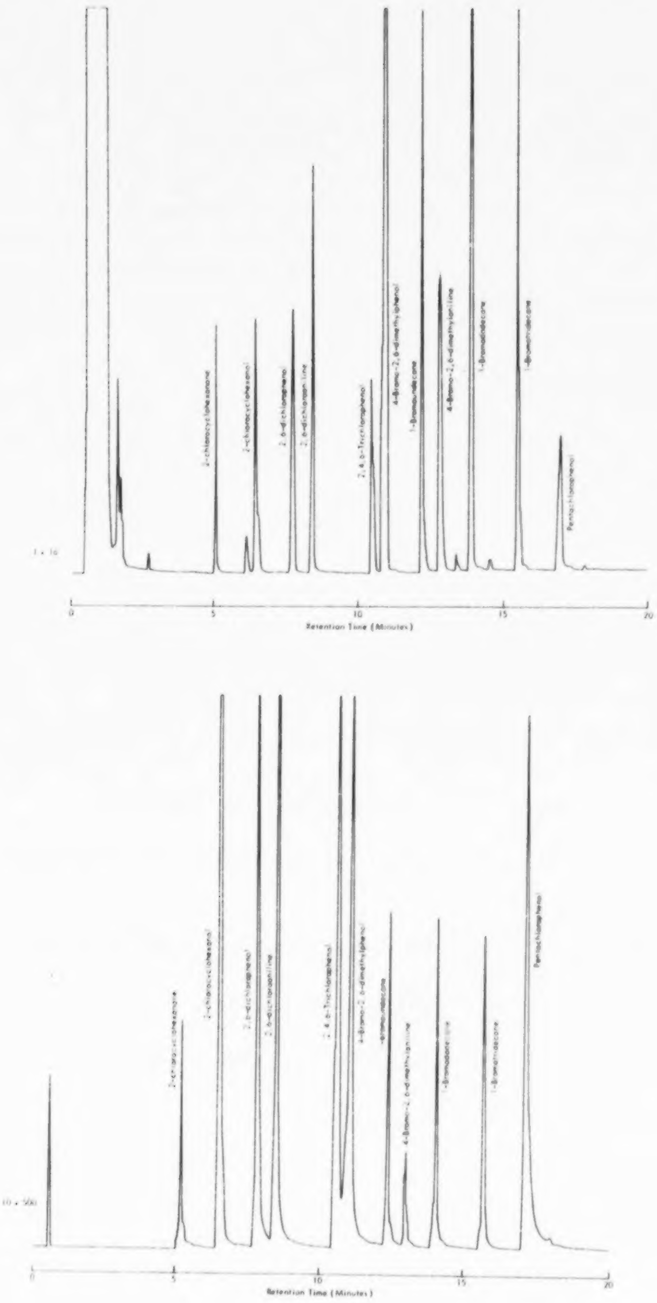


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Figure 33. HGRC/Hall-FID chromatogram of the capillary column performance standard.

TABLE 8. TARGET PAH AND PHTHALATE COMPOUNDS

PAHs	Phthalates
naphthalene	dimethylphthalate
acenaphthylene	diethylphthalate
acenaphthene	di-n-butylphthalate
fluorene	butylbenzylphthalate
phenanthrene	bis(2-ethylhexyl)phthalate
anthracene	di-n-octylphthalate
fluoranthene	
pyrene	
chrysene	
benzo[*k*]fluoranthene	
benzo[*a*]pyrene	
dibenz[*a*,*h*]anthracene	
benzo[*g*,*h*,*i*]perylene	

TABLE 9. INSTRUMENT AND OPERATING PARAMETERS FOR SCANNING HRGC/MS ANALYSIS

Instrument	Finnigan MAT 311-A/Incos
Column	15-m fused silica, wall-coated with SE-54 or DB-5
Column temperature	80°C for 2 min, then to 325°C at 10°C/min
Carrier gas	helium at 2.5 psi
Injector	J & W on-column (1 µl injection)
Scan range	m/e 32-425
Scan rate	1.5 sec/scan

The PAHs, phthalates and surrogate compounds were identified using three extracted ion current plots (EICPs) for each specific compound. The criteria for compound identification were coincident peaks in all EICPs at the appropriate retention time with the characteristic response ratios. Compounds identified were quantitated by comparing the EICP response for the most abundant ion with the most abundant ion of the internal standard (anthracene-d_{10}) and using the response factor for these two ions determined from the standard solutions.

FLUE GAS EXTRACT CLEANUP

All flue gas extracts were cleaned by adsorption chromatography prior to scanning HRGC/MS analysis. The results of HRGC/Hall-FID screening of extracts from Plants Nos. 1-4 and preliminary scanning HRGC/MS analysis of representative extracts from all plants indicated the need for cleanup. This was based on observations of high levels of background levels in chromatograms, poor chromatographic peak shapes characteristic of column overloading, and low recoveries of surrogates likely attributable to background interferences.

The adsorption column chromatographic procedure subsequently used for the flue gas extracts was adapted from methods developed by MRI for cleanup of sludge extracts.[4] Twenty-gram aliquots of freshly prepared silica gel (70 to 230 mesh, Soxhlet extracted with dichloromethane dried at 110°C and deactivated with 1% water) were placed in 14.5 x 250 mm chromatography columns containing hexane. The individual flue gas extracts were added to 2-g aliquots of silica gel and evaporated to dryness. The extracts were then placed at the top of the columns and eluted according to the following scheme.

Fraction 1 = 20 ml hexane
Fraction 2 = 80 ml hexane
Fraction 3 = 50 ml 10% benzene in hexane
Fraction 4 = 50 ml 50% benzene in hexane
Fraction 5 = 150 ml 10% acetone in benzene
Fraction 6 = 40 ml methanol

Fraction 1 from each column was discarded. The remaining fractions were screened by HRGC/Hall-FID to estimate the degree of cleanup and recovery of the surrogate compounds. Fractions 3-6 for flue gas extracts from Plant Nos. 1 and 2 were composited prior to scanning HRGC/MS analysis. Fraction 2 from these extracts were analyzed individually since HRGC/Hall-FID screening indicated the presence of significant interferences. Fractions 2-6 were composited for extracts from Plants Nos. 3-7 prior to scanning HRGC/MS analysis. Table 10 shows the recoveries observed for the surrogate compounds, the target PAH compounds, and selected PCDD and PCDF isomers spiked into hexane.

TABLE 10. RECOVERIES FOR COMPOUNDS CHROMATOGRAPHED ON SILICA GEL BY THE PROCEDURE USED TO CLEAN FLUE GAS EXTRACTS

Compound	% Recovery[a]
Naphthalene-d_8	71
1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	83
Acenaphthylene	55
Acenaphthene	69
Fluorene	76
Pentachlorophenol-$^{13}C_6$	37
Phenanthrene	87
Anthracene	81
Fluoranthene	87
Pyrene	91
3,4,3,4'-Tetrachlorobiphenyl-d_6	88
Chrysene-d_{12}	57
Benzo[*a*]pyrene	95
Dibenz[*a*,*h*]anthracene	88
2-Chlorodibenzo-*p*-dioxin	80
2,7-Dichlorodibenzo-*p*-dioxin	89
1,2,4-Trichlorodibenzo-*p*-dioxin	88
1,2,3,4-Tetrachlorodibenzo-*p*-dioxin	104
Octachlorodibenzofuran	104

[a] Spike level was 50 μg.

HRGC/MS-SIM

PCBs

Extracts of grab samples from Plants Nos. 1, 2, and 3 were analyzed for PCBs using a specialized HRGC/MS-SIM procedure, selected mass range scan HRGC/MS. That is, the mass spectrometer was scanned over the m/e range of the molecular cluster for each of the chlorobiphenyls. The specific operating parameters are listed in Table 11. In order to improve sensitivity, scan ranges were switched according to a pre-set program during the course of the HRGC/MS run so that only two sets of chlorobiphenyl compounds were analyzed simultaneously. The specific time points for switching the ion sets were selected based on the elution times for chlorobiphenyl compounds in a mixture of Aroclor® 1248, 1254, and 1260. A chromatogram of this mixture analyzed by scanning HRGC/MS is shown in Figure 34. Ions for monochloro- and dichlorobiphenyl were monitored from the initiation of the run until a time after the elution of monochlorobiphenyl but before the elution of trichlorobiphenyl. At that time, the ion set was switched to monitor for dichloro- and trichlorobiphenyl. This sequence was continued throughout each run. Hence, the last set of ions monitored were for nonachlorobiphenyls and decachlorobiphenyl. Positive responses to any of the PCB isomers in the composite extracts were confirmed when the peaks for the ion plots for two ions were coincident with responses in the proper ratios. PCB isomers identified were quantitated using area response factors for specific isomers with the same chlorine number. Standard solutions containing the isomers listed in Table 12 were analyzed daily at concentrations of 10, 100, and 250 pg/µl for each specific isomer.

Aliquots of the grab sample extracts from Plants Nos. 1, 2, and 3 were combined to form 5-day composites prior to PCB analysis to reduce the number of extracts analyzed. If PCBs had been detected in any of the 5-day composites, the extracts from which those composites were prepared would have been analyzed individually.

The extracts of grab samples from Plants Nos. 4-7 and the flue gas and plant background air samples from all plants were analyzed by HRGC/MS-SIM using conventional SIM procedures. The instrument and operating parameters are listed in Table 13. The analyses were completed in two runs. Mono- through trichlorobiphenyls were determined in the first run and tetra- through decachlorobiphenyls were analyzed in a second run.

The mixed Aroclor standard was used to identify the characteristic retention windows for PCB isomers. At least two different levels of specific PCB isomers were analyzed each day to determine area response factors for quantitation.

TABLE 11. INSTRUMENTAL PARAMETERS AND MASS RANGES USED FOR HRGC/MS-SIM ANALYSES OF PCBs

Instrument	Finnigan 4024
Column	15 m fused silica, wall-coated with DB-5
Column temperature	80°C for 2 min, then to 325°C at 8°C/min
Carrier gas	helium at 2.5 psi
Injector	J&W on-column (1 μl injection)
Scan rate	1 sec/scan
Scan ranges	

No. chlorines	Mass range scan (amu)	Retention time monitored (min)[a]
1	187.5 - 188.5	13.0 - 14.5
2	221.5 - 226.5	13.0 - 14.5
3	255.5 - 262.5	13.0 - 16.9
4	289.5 - 298.5	14.5 - 18.2
5	323.5 - 334.5	16.9 - 20.0
6	357.5 - 366.5	18.2 - 22.2
7	391.5 - 400.5	20.0 - 23.1
8	425.5 - 434.5	22.2 - 25.0
9	459.5 - 468.5	23.1 - 26.6
10	493.5 - 502.5	25.0 - 26.6

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[a] Determined by analyzing a mixed Aroclor standard and scanning HRGC/MS.

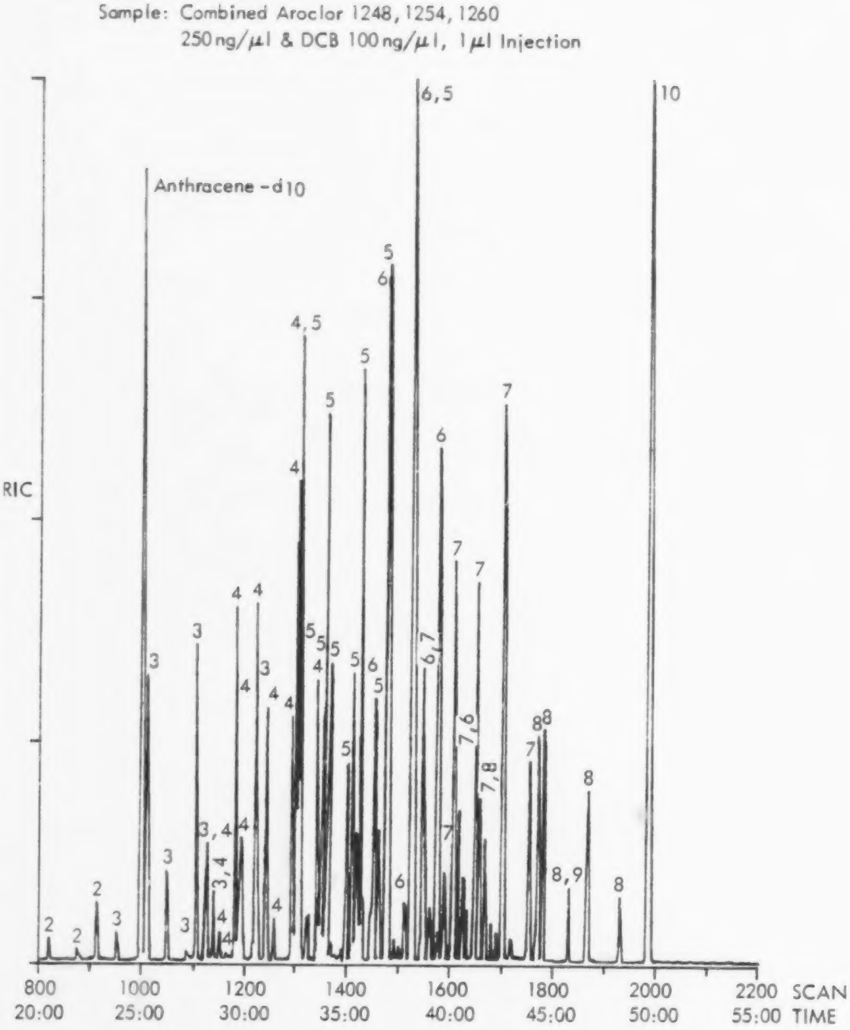

Figure 34. Mixed Aroclor standard used to establish retention windows for HRGC/MS-SIM analyses of PCBs.

TABLE 12. PCB COMPOUNDS USED FOR QUANTITATION STANDARDS

4,4'-Dichlorobiphenyl
2,3,5'-Trichlorobiphenyl
2,4,2',4'-Tetrachlorobiphenyl
2,3,4,5,6-Pentachlorobiphenyl
2,3,4,2',3',4'-Hexachlorobiphenyl
2,3,4,5,6,2',5'-Heptachlorobiphenyl
2,3,4,5,2',3',4',5'-Octachlorobiphenyl
Decachlorobiphenyl

TABLE 13. INSTRUMENT AND OPERATING PARAMETERS FOR HRGC/MS-SIM ANALYSES OF PCBs IN ALL FLUE GAS AND PLANT BACKGROUND AIR SAMPLES AND GRAB SAMPLES FROM PLANTS NOS. 4-7

Instrument	Finnigan MAT 311-A Incos
Column	15 m fused silica, wall-coated with DB-5
Column temperature	80°C hold 2 min, then to 325°C at 10°C/min
Carrier gas	helium at 2.5 psi
Injector	J&W on-column (1 µl injection)
Ions	

Chlorine No.	Ions (m/e)
1	188.0/190.0
2	222.0/224.0
3	255.9/257.9
4	291.9/293.9
5	325.9/327.9
6	357.9/359.8
7	393.8/395.8
8	427.7/429.7
9	461.7/463.7
10	497.7/499.7

The flue gas extracts required additional cleanup prior to HRGC/MS-SIM analysis for PCBs. Each individual extract was diluted to 5 ml with cyclohexane and washed with 5 ml of concentrated sulfuric acid for approximately 30 sec. The phases were allowed to separate and the organic layer was removed. The H_2SO_4 layer was extracted with 5 ml of fresh cyclohexane. The cyclohexane was separated, combined with the original cyclohexane fraction and concentrated to 1.0 ml. The recoveries for specific PCB isomers spiked into cyclohexane and treated by the acid wash procedures are shown in Table 14.

TABLE 14. RECOVERY OF PCB ISOMERS FROM SULFURIC ACID TREATED EXTRACTS

Compound	Recovery (%)
2,4,2',4'-tetrachlorobiphenyl	74, 70[a]
2,3,4,5,6-pentachlorobiphenyl	97, 92
2,3,4,2',3',4'-hexachlorobiphenyl	86, 91
2,3,4,5,6,2',5'-heptachlorobiphenyl	85, 85
2,3,4,5,2',3',4',5'-octachlorobiphenyl	78, 94
decachlorobiphenyl	85, 86

a Duplicate determinations.

PCDDs/PCDFs

Sample extracts were also analyzed by HRGC/MS-SIM for PCDDs and PCDFs. The instrument and operating parameters are listed in Table 15. Perfluorokerosene (PFK) was used to obtain stable mass assignments during PCDD and PCDF analyses. Analyses for the entire range of PCDDs and PCDFs required four injections of each extract. Mono- through tri- PCDDs and PCDFs were determined in the first run. Three subsequent runs were used to determine tetrachloro compounds, penta- and hexachloro compounds, and hepta- and octachloro compounds, respectively.

TABLE 15. INSTRUMENT AND OPERATING PARAMETERS FOR HRGC/MS-SIM ANALYSES OF PCDDs/PCDFs

Instrument	Finnigan MAT 311-A/Incos
Column	15-m fused silica, wall-coated with DB-5
Column temperature	80°C hold 2 min, then to 325°C at 10°C/min
Carrier gas	helium at 2.5 psi
Injector	J&W on-column (1 µl injection)

Chlorine No.	Dioxins (m/e)	Furans (m/e)	PFK (reference)
1	218.0/220.0	202.0/204.0	242.9
2	252.0/254.0	242.0/244.0	
3	285.9/287.9	269.9/271.9	
4	319.9/321.9	303.9/305.9	331.0
5	353.9/355.9	337.9/339.9	380.8
6	389.8/391.8	373.8/375.8	
7	423.8/425.8	407.8/409.8	430.7
8	457.7/459.7	441.7/443.7	

Five-day composites of grab sample and flue gas sample extracts were prepared for each plant for PCDD and PCDF analyses. Potential PCB interferences were removed from the composite flue gas samples by fractionation on alumina columns (8 x 1.4 cm) according to the procedure outlined in the U.S. EPA Method 613. The alumina was activated at 130°C for at least 24 hr before use. The columns were packed, and eluted with 50 ml of hexane before the sample was added to the top of the column. Each column was then eluted with 50 ml of 3% dichloromethane in hexane and the eluent was discarded. The column was then eluted with 50 ml of 20% dichloromethane in hexane which was collected and concentrated to 1.0 ml for analyses. The recoveries of duplicate blanks spiked with 50 ng of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin were 100 and 99%.

SECTION 7

FIELD TEST DATA

This section presents summaries of the flue gas sampling data, unit operating parameters, and particulate control device operating data for the seven coal-fired utility boilers.

PLANT NO. 1

A summary of the daily data for flue gas sampling as calculated from the field data sheets is presented in Table 16. The data listed are corrected to standard conditions, i.e., 20°C and a barometric pressure of 29.92 in. (1.0 atm.) of mercury. Events that may have created uncertainties are noted. Table 17 is a summary of the plant background air sampling data.

Table 18 summarizes the boiler process data monitored hourly during the flue gas sampling periods. The parameters recorded include the turbine steam flow (lb/hr), flue gas temperatures from the two preheaters in °F, gross output (Mw), opacity in the combined stack (%), and coal usage (tons/hr). All information was collected in the control room from meters or the computer output. Table 19 lists the inoperable fields in each of the ESP stages during the test period and also notes the average ESP operating conditions. ESP performance was monitored from the meters on the ESP control boards.

Table 20 summarizes the major variations in operating conditions during the test periods. For the most part, operating conditions were very stable. Slight variations in steam flow and gross output were related to variations in the Btu value of the coal feed.

The average performance and ultimate fuel contents of the coal used to operate this plant during the 5-day test period are shown in Table 21.

TABLE 16. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 1

Test No.	Sampling Location	Sample volume		Gas composition[a]				Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Flue gas flow[b]			Isokinetic rate (%)
		dscf	dscm	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)					acfm	dscfm	dscmm	
1	A	344.50	9.80	5.2	14.0	ND[c]	0.4	322.9	30.57	10.74	101.9	5,428,000	3,266,000	92,500	95.1
	B	339.27	9.61	5.2	14.0	ND	0.4	304.2	30.57	10.59	98.05				94.9
2	A	359.19	10.17	5.3	14.4	ND	2.3	311.6	30.35	10.49	96.22	5,238,000	3,166,000	89,650	103.0
	B	364.11	10.31	5.3	14.4	ND	2.3	317.3	30.35	10.30	96.77				104.3
3	A	372.22	10.54	5.3	13.2	6.9	1.7	310.4	30.59	10.09	77.81	5,364,000	3,257,000	92,200	104.3
	B	326.74	9.25	5.3	13.2	6.9	1.7	310.0	30.59	10.97	99.78				90.6
4	A	354.76	10.05	5.6	13.7	6.5	1.1	293.9	30.43	10.32	88.98	4,796,000	2,990,000	84,680	105.9
	B	293.11	8.30	5.6	13.7	6.5	1.1	295.7	30.43	11.81	87.72				90.5
5	A[d]	-	-	-	-	-	-	-	-	-	-				-
	B	374.67	10.61	5.7	13.8	7.4	4.9	299.6	30.31	10.36	99.87	2,711,000	1,688,000	47,800	100.7

[a] Average values for duration of test.

[b] Sum of the flow through the total outlet.

[c] ND = not detected.

[d] Gasket slippage created a post leak rate of 0.7 cfm. This test was not valid.

TABLE 17. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 1

Test	Volume	
	dscf	dscm
1	387.71	10.98
2	387.31	10.97
3	435.26	12.33
4	443.46	12.56
5	388.23	10.99
6[a]	521.47	14.77

[a] Test No. 6 was a lab background sample collected in the same manner as the intake air for Test Nos. 1 through 5.

TABLE 18. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 1

Test	Gross output (Mw)	Steam flow (10,000 lb/hr)	Gas temperature from preheaters (°F) Unit 11	Gas temperature from preheaters (°F) Unit 12	Opacity (%)	Coal usage (tons/hr)
1 - average	611	445	340	327	4.1	353
range	598-628	437-464	340-352	325-338	3.9-5.1	N/A
2 - average	612	445	338	330	4.9	422
range	580-635	425-457	330-352	326-350	4.6-5.9	N/A
3 - average	615	452	330	331	4.3	400
range	553-636	401-466	328-347	325-339	3.7-5.1	N/A
4 - average	555	404	322	316	4.9	364
range	533-573	391-418	319-322	314-321	4.3-5.8	N/A
5 - average	610	450	331	323	4.7	400
range	584-623	477-461	327-333	320-324	4.6-5.2	N/A

TABLE 19. ELECTROSTATIC PRECIPITATOR OPERATING INFORMATION, PLANT NO. 1

A. Number of fields inoperable during flue gas test periods

Primary unit	9-10[a]
Secondary unit	1-2[b]

B. Average operating conditions

	Primary unit	Secondary unit
Primary voltage	300-320 AC-v	360-380 AC-v
Primary amperes	N/A	140-160 AC-amp
Bushing-1 MA	N/A	240-260 DC-amp
DC kilovolts	N/A	36-40 DC-kv
Bushing-2 MA	N/A	280-320 DC-amp

[a] 9 Fields inoperable day 1 and day 2.
10 Fields inoperable day 3 through day 5.

[b] 1 Field inoperable day 1 to day 5.
2 Fields in operable day 4 and day 5.

TABLE 20. LOG OF SYSTEM CHANGES, UPSETS AND BREAKDOWNS DURING FLUE GAS TESTING, PLANT NO. 1

Test Day 1 -	Relatively constant operating conditions.
Test Day 2 -	Pulverizer no. 15 was removed from service causing a lower output level in the final minutes of the test period.
Test Day 3 -	At the beginning of the test period the system was gradually normalizing after a load drop anticipator problem had earlier caused a sudden drop in the output level. Later, a temporary power reduction was caused by a maintenance check of turbine valves. Later in the period, pulverizer no. 15 was removed from operation causing a lower output level for the remainder of day 3 and day 4.
Test Day 4 - and Test Day 5	A brief output reduction was caused by the temporary cut off of a pulverizer unit, otherwise, both days were relatively stable.

TABLE 21. PROXIMATE AND ULTIMATE ANALYSIS RESULTS FOR COAL, PLANT NO. 1

	Average[a]	Standard deviation
Proximate analysis		
As received		
Moisture (%)	22.69	1.65
Ash (%)	13.91	1.18
Volatile (%)	31.41	1.56
Fixed carbon (%)	31.98	0.48
Sulfur (%)	0.45	0.12
Heat of combustion (Btu/lb)	7,842	383
Dry basis		
Ash (%)	18.00	1.56
Volatile (%)	40.62	1.43
Fixed carbon (%)	41.38	0.54
Sulfur (%)	0.58	0.16
Heat of combustion (Btu/lb)	10,142	381
A and M free Btu (Btu/lb)	12,367	363
Ultimate analysis		
Hydrogen (%)	3.00	0.17
Carbon (%)	59.47	2.37
Nitrogen (%)	0.72	0.23
Oxygen (%)	18.20	1.64
Total chlorine (ppm)	269	187

[a] Results for five daily composite coal samples.

PLANT NO. 2

The daily data summaries for flue gas sampling at Plant No. 2 are shown in Table 22. Table 23 is a summary of the volumes for plant background air samples taken during the flue gas testing.

Table 24 is a summary of the process data monitored during the flue gas test period. The parameters monitored include gross output (Mw), steam flow (lb/hr), outlet gas temperature from preheaters 4A and 4B (°F), and opacity percentage (from a meter in the stack). All data were obtained from meters and recorders in the control room or from the shift operator.

Table 25 is a summary of the ESP operating conditions during the five flue gas test runs. Primary voltage (AC-v), primary current (AC-amp), precipitator current (DC-amp), and spark rate were read directly from the ESP control panels. All sections of the ESP were operable during the test periods.

Table 26 is a log of system changes, upsets, and breakdowns during the flue gas test periods. In general, operations were quite stable except for variations in power output and excess oxygen caused by variations in coal quality. Power cutbacks due to reduced demand were made on days 1, 3, and 5. An excesive spark rate and a drop in precipitator and primary current were noted in the ESP on day 5.

Table 27 is a summary of the average proximate and ultimate fuels content of the coal used at Plant No. 2 during the 5-day testing period.

PLANT NO. 3

Table 28 presents the daily data summaries for the flue gas sampling at Plant No. 3. A summary of the volumes for plant background air samples are shown in Table 29.

Table 30 summarizes boiler operating conditions during the test period. Continuous process monitors were available in the boiler room. These included steam flow, pressure, temperature, megawatt output, feedwater temperatures, pulverizer operation, ESP data, opacity (based on a continuous and 6-min average transmissometer in the ESP outlet), and flue gas temperatures.

Boiler operation remained steady and relatively unchanged throughout the 5 days of testing. Only minor adjustments occurred due to events such as one high opacity episode, changes in coal properties, and regular adjustments required when returning the boiler to typical operating parameters.

Table 31 summarizes the ESP operating conditions during the test for Plant No. 3. During the test period, the ESP performed according to specifications. No breakdowns or disruptions occurred.

TABLE 22. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 2

Test No.	Sampling Location	Sample volume		Gas composition[a]				Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Gas flow[b]			Isokinetic rate (%)
		dscf	dscm	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)					acfm	dscfm	dscmm	
1	North	329.41	9.33	4.5	17.1	119.9	0.4	663.5	31.34	6.86	66.25	1,192,000	504,400	14,280	101.6
	South	240.53	6.81	4.5	17.1	119.9	0.4	657.4	31.34	7.64	66.23				105.1
2	North	251.52	7.12	2.6	17.5	143.8	0.6	657.0	30.93	8.44	68.48	1,259,000	513,100	14,530	109.4
	South	242.11	6.86	2.6	17.5	143.8	0.6	668.0	30.93	8.62	69.17				104.0
3	North	318.86	9.03	3.7	15.4	19.4	-	657.2	30.76	7.33	70.25	1,235,000	525,000	14,870	102.5
	South	317.15	8.98	3.7	15.4	19.4	-	648.9	30.76	7.09	67.0				104.2
4	North	315.50	8.93	3.4	15.7	31.7	0.4	654.9	30.65	7.33	67.95	1,246,000	531,700	15,060	104.1
	South	326.63	9.25	3.4	15.7	31.7	0.4	652.3	30.66	7.30	70.53				102.0
5	North	319.74	9.05	3.0	15.8	71.7	0.2	651.9	30.81	7.45	67.25	1,229,000	526,300	14,900	106.3
	South	323.04	9.15	3.0	15.8	71.7	0.2	651.9	30.81	7.00	69.33				102.1

[a] Average values for duration of test.

[b] Sum of flow through the total outlet.

TABLE 23. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 2

Test	Volume dscf	Volume dscm
1	368.33	10.43
2	379.77	10.76
3	403.31	11.42
4	407.89	11.55
5	378.58	10.72

TABLE 24. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 2

Test	Gross output (Mw)	Steam flow (10,000 lb/hr)	Preheater outlet gas temperatures (°F) Unit 4A	Preheater outlet gas temperatures (°F) Unit 4B	Opacity (%)
1 - average	268	188	300	300	40
range	221-270	150-190	290-305	280-315	20-60
2 - average	268	192	300	305	50
range	262-271	190-195	295-305	300-310	20-90
3 - average	260	190	277	280	45
range	200-265	135-192	275-280	265-285	25-80
4 - average	265	175	285	287	45
range	232-268	168-196	280-290	285-290	25-80
5 - average	260	191	285	290	40
range	235-270	160-195	275-290	275-300	25-80

TABLE 25. SUMMARY OF ELECTROSTATIC PRECIPITATOR OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 2

Test	Primary voltage (AC-v)	Primary current (AC-amp)	Precipitator current (DC-amp)	Spark rate (sparks/min)
1 - average	200	140	0.9	90
range	160-260	110-220	0.5-1.4	0-175
2 - average	200	160	0.9	80
range	160-260	90-220	0.5-1.2	0-150
3 - average	200	160	0.9	60
range	160-270	90-220	0.4-1.3	0-120
4 - average	200	170	0.9	70
range	120-270	110-220	0.5-1.4	0-120
5 - average	200	110	0.5	150
range	150-250	50-210	0.3-1.0	0-250

TABLE 26. LOG OF SYSTEM CHANGES, UPSETS, AND BREAKDOWNS DURING FLUE GAS TESTING, PLANT NO. 2

Test Day 1 -	Operating conditions were very stable except for two cutbacks in power generation due to reduced demand. Excess oxygen varied widely when the cutbacks were made.
Test Day 2 -	Operating conditions were very stable.
Test Day 3 -	A brief upset was caused by a pulverizer outage. The power output was reduced during the last 2 hr of the test period.
Test Day 4 -	Power output varied somewhat due to changes in coal characteristics. One brief upset was caused by a pulverizer outage.
Test Day 5 - (Sunday)	ESP operating conditions changed significantly about 4 hr into the test period. The spark rate was excessive and the precipitator current and primary current decreased. Other operating conditions were relatively stable except for a power decrease later in the test period.

TABLE 27. PROXIMATE AND ULTIMATE ANALYSIS RESULTS FOR COAL, PLANT NO. 2

	Average[a]	Standard deviation
Proximate analysis		
As received		
Moisture (%)	7.05	0.36
Ash (%)	13.55	1.34
Volatile (%)	29.42	1.04
Fixed carbon (%)	49.98	0.99
Sulfur (%)	1.89	0.22
Heat of combustion (Btu/lb)	11,576	259
Dry basis		
Ash (%)	14.58	1.45
Volatile (%)	31.64	1.15
Fixed carbon (%)	53.77	0.98
Sulfur (%)	2.03	0.23
Heat of combustion (Btu/lb)	12,492	305
A and M free Btu (Btu/lb)	14,624	116
Ultimate analysis		
Hydrogen (%)	4.53	0.25
Carbon (%)	66.14	1.82
Nitrogen (%)	1.21	0.05
Oxygen (%)	11.48	2.85
Total chlorine (ppm)	225	268

[a] Results for five daily composite coal samples.

TABLE 28. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 3

Test No.	Sampling Location	Sample volume		Gas composition[a]				Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Gas flow[b]			Isokinetic rate (%)
		dscf	dscm	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)					acfm	dscfm	dscmm	
1	A	320.92	9.09	4.9	13.8	17.7	1.6	300.7	30.33	6.46	54.68	919,300	576,400	16,320	96.1
	B	345.90	9.80					300.6	30.37	6.49	55.88				100.5
2	A	341.32	9.67	5.2	13.7	14.6	0.3	297.6	30.28	6.99	54.95	916,000	571,500	16,180	101.2
	B	350.96	9.94					300.5	30.28	6.98	55.23				104.8
3	A	340.21	9.63	5.0	14.1	11.7	1.6	294.3	30.33	7.42	56.10	927,400	573,700	16,240	99.4
	B	347.01	9.83					300.5	30.33	7.57	55.45				104.4
4	A	347.75	9.85	4.9	14.1	8.8	0.2	290.0	30.38	7.88	56.03	931,500	576,100	16,310	101.8
	B	356.59	10.10					297.9	30.38	7.69	56.03				106.1
5	A	337.44	9.56	5.0	13.8	10.3	0.5	287.0	30.25	7.90	54.85	921,400	573,000	16,230	100.3
	B	343.36	9.72					294.9	30.25	7.81	55.98				101.7

[a] Average values for duration of test.

[b] Sum of the flow through the total outlet.

TABLE 29. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 3

Test	Volume	
	dscf	dscm
1	308.66	8.74
2	328.67	9.31
3	309.43	8.76
4	329.83	9.34
5	312.96	8.86
6[a]	300.22	8.50
7[a]	320.10	9.10

[a] Lab background samples.

TABLE 30. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 3

Test	Gross output (Mw)	Steam flow (10,000 lb/hr)	Gas temperature from preheaters (°F)	Opacity (%)	Coal usage (tons/hr)
1 - average	121	87	308	14	46
range	120-122	86-88	300-310	11-26	N/A[a]
2 - average	123	87	307	10.5	42
range	151-125	86-88	300-310	9-18	N/A
3 - average	121	87	310	9.9	46
range	120-123	86-88	305-312	5-19	N/A
4 - average	121	88	308	15	47
range	120-122	88-89	300-312	12-17	N/A
5 - average	121	87	304	11	46
range	100-123	72-88	292-310	6-20	N/A

[a] NA = not available.

TABLE 31. ESP OPERATING CONDITIONS, PLANT NO. 3

Test	Spark rate[a] (sparks/min)	Primary current (AC-amp)	Primary voltage (AC-v)
1 - average	100	134	258
range	88-112	80-175	215-300
2 - average	88	136	256
range	92-112	80-185	220-300
3 - average	87	129	258
range	92-112	70-180	220-295
4 - average	99	134	269
range	90-112	80-185	240-300
5 - average	87	140	264
range	84-112	80-185	250-300

[a] All fields were operational during the test. Each field was periodically shut off about each half-hour. Only one field was off at a time.

Manufacturer: American Standard
Design volume, acfm: 475,000
Design temperature, °F: 300
Design inlet concentration: 3.88 g/acf
Cells per chamber: 4
Fields deep: 4/precipitator
Gas passages/field: 74
Collecting surfaces: 75
Collecting surface spacing: 9 in.
Face area/precipitator, ft^2: 1,665
Total surface, ft^2: 153,290
Gas velocity, fps: 4.75
Retention time, sec: 7.29

The results of proximate and ultimate fuels analysis on coal and ashes from Plant No. 3 are shown in Table 32. Since bottom ash, ESP ash, and economizer ash were all sampled at Plant No. 3 as dry ash prior to quenching, fuels analyses were conducted to allow examination of possible correlation of specific compounds with gross characteristics.

TABLE 32. PROXIMATE AND ULTIMATE ANALYSES FOR COAL, BOTTOM ASH, FLY ASH, AND ECONOMIZER ASH, PLANT NO. 3

	Coal[a]	Bottom Ash[b]	Fly Ash[b]	Economizer Ash[b]
Proximate Analysis				
Reported as received				
Moisture (%)	6.34 ± 2.16	14.01	0.02	0.10
Ash (%)	13.40 ± 1.08	81.54	90.14	74.60
Volatile (%)	31.91 ± 1.11	0.33	1.61	0.01
Fixed carbon (%)	48.75 ± 1.85	4.13	8.23	25.30
Sulfur (%)	0.88 ± 0.09	0.09	0.22	0.12
Heat of combustion (Btu/lb)	11,660 ± 430	66	1,304	1,405
Dry basis				
Ash (%)	14.32 ± 1.35	94.82	90.15	74.67
Volatile (%)	34.05 ± 0.75	0.38	1.61	0.01
Fixed carbon (%)	51.63 ± 0.86	4.80	8.23	25.32
Sulfur (%)	0.94 ± 0.09	0.11	0.23	0.12
Heat of combustion (Btu/lb)	12,446 ± 228	77	1,304	1,407
A and M free Btu (Btu/lb)	14,526 ± 77	1,492	13,241	5,553
Ultimate Analysis				
Dry basis				
Hydrogen (%)	4.63 ± 0.25	0.01	0.01	0.34
Carbon (%)	70.04 ± 0.87	3.60	9.47	12.42
Nitrogen (%)	0.55 ± 0.38	0.68	0.26	0.61
Oxygen (%)	9.53 ± 0.47	0.79	0.00	11.84
Total chlorine (ppm)	528 ± 260	NA[c]	NA	NA

a Results from five daily composite samples.

b Results from a single 5-day composite sample.

c Not analyzed.

PLANT NO. 4

Table 33 presents the daily data summaries for the flue gas sampling at Plant No. 4. The air volumes sampled for plant background air are shown in Table 34.

Table 35 summarizes the process data monitored during the flue gas test period. The parameters monitored include gross output (Mw), steam flow (lb/hr), the gas temperature from the heaters (east, middle, and west in °F), and opacity percentage (from a meter in the stack). All data were obtained from meters and recorders in the control room.

The ESP operating conditions during the five flue gas test runs are summarized in Table 36. Primary current (AC-amp), primary voltage (AC-v), precipitator current (DC-mA), and precipitator voltage (DC-kv) were read directly from meters in the ESP control room. The spark rates were calculated from reading on the total sparks counter for each bus section. All sections were operable during the test periods except one section during Day Nos. 3, 4, and 5. Table 34 also identifies the individual bus sections having a significant sparking rate during the test periods. The sections not listed (most notably the various sections in the D and E fields) had sparking rates of approximately zero sparks per minute.

Table 37 is a log of system changes, upsets, and breakdowns during the flue gas test periods. During test days 2 and 3, operating conditions were very constant. On days 1 and 4 a change in pulverizer units caused a period of variation. During day 5 the power output was changed several times due to varying demand, producing a number of changes in operating parameters.

Table 38 is a summary of the average proximate and ultimate fuels content of the coal used at Plant No. 4 during the testing period.

PLANT NO. 5

The daily data summaries for flue gas sampling at Plant No. 5 are shown in Table 39. The volumes sampled for plant background air are shown in Table 40.

Table 41 lists the process data monitored during the flue gas test period. Parameters observed included gross output (mw), steam flow (lb/hr), preheater outlet temperature, opacity, oxygen, coal usage and SO_2 and NO emissions. All information was obtained from meters in the control room.

Electrostatic precipitator operating conditions during the test period are summarized in Table 42. Parameters observed were primary voltage (AC-V), primary current (AC-amp) and spare rate. Values were obtained from meters on the ESP control units.

TABLE 33. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 4

Test No.	Sampling Location	Sample volume		Gas composition[a]				Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Gas flow[b]			Isokinetic rate (%)
		dscf	dscm	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)					acfm	dscfm	dscmm	
1	A[c]	346.10	9.80	6.6	12.2	9.2	1.3	336.0	30.33	7.71	57.38	1,720,000	1,037,00	29,360	102.6
	B[d]	296.88	8.41					334.3	30.33	6.50	54.18				92.6
2	A[e]	341.10	9.66	6.5	12.4	17.0	2.7	342.1	29.36	7.93	58.08	1,711,000	1,020,000	28,890	101.6
	B	300.03	8.50					338.2	30.34	7.57	52.95				96.4
3	A	344.43	9.76	6.5	12.3	20.1	1.9	335.3	30.71	7.88	56.27	1,672,000	1,002,000	28,370	104.9
	B	307.37	8.70					334.8	30.78	8.01	52.22				100.1
4	A	336.66	9.53	6.4	12.3	24.4	1.2	342.2	30.43	8.40	56.90	1,719,000	1,012,000	28,665	102.9
	B[f]	307.90	8.72					336.5	30.43	8.10	54.62				97.8
5	A	280.90	7.95	8.6	11.1	12.2	0.7	336.1	30.16	7.31	47.47	1,450,000	867,100	24,550	101.9
	B[f]	269.58	7.63					328.7	30.16	7.56	46.62				98.2

a Average values for duration of test.

b Sum of the flow through the total outlet.

c Flexible line was discovered to be disconnected during the change from Port 1 to 2. The test is likely valid.

d Post leak rate was 0.06 cfm. These data were corrected for the leak according to EPA Method 5 procedures. The validity of the test is questionable.

e Port change error sampled 3.5 of lowest points in Port 1 instead of Port 3. The test is likely valid.

f The flexible line was found to be kinked twice during the test. However, the test is considered valid based on close agreement of sample moisture.

g Post leak rate was 0.023 cfm, presenting a potential error of approximately 3%. The test is considered valid.

TABLE 34. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 4

Test	Volume	
	dscf	dscm
1	277.821	7.868
2	264.785	7.499
3	261.126	7.395
4	202.408	5.732
5	284.516	8.058
6[a]	309.131	8.755
7[a]	337.028	9.545

[a] Lab background samples.

TABLE 35. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 4

Test	Gross output (Mw)	Steam flow (10,000 lb/hr)	Gas temperature from heaters (°F) east	middle	west	Opacity (%)
1 - average	209	148	345	345	320	12
range	182-209	126-149	340-350	340-345	315-320	7-12
2 - average	212	147	348	350	320	10
range	212-213	146-147	340-350	345-355	320	8-13
3 - average	214	146	345	345	320	11
range	213-215	145-148	340-345	345-350	315-320	5-14
4 - average	213	148	350	350	325	10
range	212-215	145-151	340-360	345-360	310-330	8-12
5 - average	152	105	330	345	310	9
range	125-155	88-108	315-340	320-345	295-315	3-12

TABLE 36. SUMMARY OF ELECTROSTATIC PRECIPITATOR OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 4

Test	Sections operating	Sections with active sparking	Spark rate of active sparking sections (sparks/min)	Primary current (AC-amp)	Primary voltage (AC-v)	Precipitator current (DC-mA)	Precipitator voltage (DC-kv)
1 - average	all	7	12	120	350	720	43
range			6-19	46-124	300-500	200-740	38-60
2 - average	all	6	13	120	350	730	43
range			8-19	58-124	280-520	340-740	38-62
3 - average	all except 1 unit	5	14	120	350	730	43
range			9-16	50-124	320-540	220-750	38-66
4 - average	all except 1 unit	4	15	120	350	730	43
range			10-19	55-124	320-500	280-740	38-62
5 - average	all except 1 unit	3	10	120	340	730	44
range			3-18	118-124	330-500	600-740	32-56

TABLE 37. LOG OF SYSTEM CHANGES, UPSETS, AND BREAKDOWNS DURING FLUE GAS TESTING, PLANT NO. 4

Test Day 1 - Almost constant operating conditions until a pulverizer burned out aout 45 min before the end of the sampling time. Operations were erratic during the last 45 min.

Test Day 2 - No upsets--very constant operating conditions.

Test Day 3 - No upsets--very constant operating conditions.

Test Day 4 - Three hours into the test an additional pulverizer was placed into service, causing temporary variations in operating parameters. Otherwise, operating conditions were very constant.

Test Day 5 - Operating parameters varied throughout the test period. The gross output changed several times due to varying demand. Excess air values varied significantly throughout the test.

TABLE 38. PROXIMATE AND ULTIMATE ANALYSIS RESULTS FOR COAL, PLANT NO. 4

	Average[a]	Standard deviation
Proximate fuel analysis		
As received		
Moisture (%)	5.90	0.76
Ash (%)	11.78	2.17
Volatile (%)	37.76	2.93
Fixed carbon (%)	44.56	2.39
Sulfur (%)	3.77	0.33
Heat of combustion (Btu/lb)	11,920	162
Dry basis		
Ash (%)	12.51	2.21
Volatile (%)	40.14	2.30
Fixed carbon (%)	47.35	2.49
Sulfur (%)	3.90	0.30
Heat of combustion (Btu/lb)	12,669	244
A and M free Btu (Btu/lb)	14,483	112
Ultimate analysis		
Hydrogen (%)	4.25	0.28
Carbon (%)	60.44	0.84
Nitrogen (%)	1.33	0.10
Oxygen (%)	9.52	2.07
Total chlorine (ppm)	359	29

[a] Results for five daily composite coal samples.

TABLE 39. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 5

Test No.	Sampling location	Sample volume dscf	Sample volume dscm	Gas composition[a] O_2 (%)	Gas composition[a] CO_2 (%)	Gas composition[a] CO (ppm)	Gas composition[a] THC (ppm)	Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Flue gas flow[b] acfm	Flue gas flow[b] dscfm	Flue gas flow[b] dscmm	Isokinetic rate (%)
1	A	334.62	9.48	6.0	13.3	12.9	0.9	300	30.53	5.5	98.95	4,125,000	2,618,000	74,100	98.0
	B	336.91	9.54					297	30.53	5.9	99.53				98.1
2	A	337.98	9.57	5.0	12.6	8.0	0.8	300	30.55	5.6	97.42	4,069,000	2,592,000	73,400	100.2
	B	340.95	9.65					298	30.55	6.0	98.40				100.1
3	A	333.51	9.44	4.9	13.1	7.3	ND[c]	303	30.64	5.6	97.00	4,075,000	2,590,000	73,300	99.8
	B	344.48	9.75					296	30.64	6.1	99.08				100.4
4	A	340.90	9.65	5.4	12.2	9.4	0.3	282	30.52	5.7	80.68	3,336,000	2,169,000	61,400	99.9
	B	341.00	9.66					274	30.52	6.2	79.87				100.4
5	A	296.48	8.40	6.1	11.2	23.6	0.1	278	30.48	5.6	69.92	2,880,000	1,872,000	53,000	99.7
	B	289.95	8.21					269	30.48	6.1	67.70				100.0

[a] Average values for duration of test.

[b] Sum of the flow through the total outlet.

[c] ND = not detected.

TABLE 40. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 5

Test	Volume	
	dscf	dscm
1	331.24	9.38
2	349.64	9.90
3	351.21	9.95
4	350.58	9.93
5	338.30	9.58

TABLE 41. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING; PLANT NO. 5

Test	Gross output (mw)	Steam flow (1,000,000 lb/hr)	Gas temperature from preheaters (°F)		Opacity[a] (%)			Oxygen[a] (%)			SO_2 (ppm)	NO (ppm)	Coal usage (tons/hr)
			A	B	Stack	A	B	Stack	A	B			
1 - Average	590	3.8	320	320	7	14	2	8.0	4.0	3.2	840	280	289
Range	510-595	3.3-3.8	310-328	310-325	4-12	9-19	0-8	7-8.5	3.8-4.2	2.3-3.2	800-840	250-360	N/A[b]
2 - Average	586	3.8	320	320	7	14	1	8.0	3.8	2.9	950	340	223
Range	580-590	3.80-3.84	302-330	302-328	3-16	7-19	0-7	7.2-9.0	3.5-4.5	2.7-3.2	9,010-1,050	250-360	N/A
3 - Average	590	3.9	328	325	7	15	1	7.5	3.7	2.8	980	390	N/A
Range	589-591	N/A	310-330	308-328	4-20	10-17	0-5	7-8	3.5-4.0	2.5-3.1	840-1,000	350-410	N/A.
4 - Average	460	3.0	300	295	6	14	1	6.5	3.5	3.0	900	340	176
Range	418-501	2.7-3.2	295-305	290-300	3-8	11-21	0.4	6-7	2.9-3.7	2.6-3.4	810-960	315-390	N/A
5 - Average	370	2.5	305	290	5	14	1	7.5	3.5	3.4	950	350	149
Range	318-400	2.0-2.6	395-310	280-300	3-8	8-18	0-2	6.5-8.5	3.1-4.4	2.7-4.5	880-1000	280-360	N/A

[a] Sections A and B are inlets to electrostatic precipitators.

[b] NA = not available.

TABLE 42. SUMMARY OF ELECTROSTATIC PRECIPITATOR OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 5

Test	Primary voltage (AC-v)	Primary current (AC-amp)	Spark rate (sparks/min)
1 - Average	200	100	25
Range	160-300	40-230	5-50
2 - Average	200	100	20
Range	180-300	35-240	1-50
3 - Average	200	90	20
Range	160-300	40-240	5-45
4 - Average	250	140	15
Range	200-320	60-240	1-40
5 - Average	250	160	15
Range	190-310	80-250	1-50

NOTE - All units were functioning during all test runs.

A summary of system changes, upsets and breakdowns is listed in Table 43. Other than a brief coal feeder breakdown on day 1, the only variations in operation were due to variations in load demand.

TABLE 43. LOG OF SYSTEM CHANGES, UPSETS, AND BREAKDOWNS DURING FLUE GAS TESTING, PLANT NO. 5

Test Day 1	- One coal feed unit stopped for about 10 min due to a stoppage 5 hr into the test. This caused a temporary reduction in output. Output was brought down during the final half hour of testing due to reduced demand.
Test Days 2 and 3	- Very stable operating conditions during the test period.
Test Days 4 and 5	- Variable output due to variations in the weekend load demand.

The results of proximate and ultimate fuels analyses of 5-day composites of coal, bottom ash, and fly ash from Plant No. 5 are summarized in Table 44.

TABLE 44. PROXIMATE AND ULTIMATE ANALYSIS RESULTS FOR COAL, BOTTOM ASH, AND FLY ASH, PLANT NO. 5

	Coal	Bottom ash	Fly ash
Proximate analysis			
Reported as received			
Moisture (%)	6.13	36.73	0.22
Ash (%)	13.81	46.31	96.59
Volatile (%)	33.30	1.95	0.28
Fixed carbon (%)	46.76	15.01	2.92
Sulfur (%)	1.81	0.21	0.10
Heat of combustion (Btu/lb)	12,121	799	432
Dry basis			
Ash (%)	14.71	73.19	96.80
Volatile (%)	35.47	3.08	0.28
Fixed carbon (%)	49.82	23.73	2.92
Sulfur (%)	1.93	0.33	0.10
Heat of combustion (Btu/lb)	12,912	1,262	433
A and M free Btu (Btu/lb)	15,140	4,708	13,529
Ultimate analysis			
Dry Basis			
Hydrogen (%)	4.15	0.21	0.06
Carbon (%)	67.17	25.63	4.10
Nitrogen (%)	1.37	0.56	0.28
Oxygen (%)	10.67	0.10	0.00
Total chlorine (ppm)[a]	780, 650	390, 500	940, 1,000

[a] Duplicate determinations.

PLANT NO. 6

The daily data summaries for flue gas sampling at Plant No. 6 are shown in Table 45. The volumes of plant background air sampled are shown in Table 46.

Table 47 lists the process data monitored during the flue gas test period. Parameters observed included gross output (mw), steam flow (lb/hr), temperature at the superheater outlets, and excess oxygen. Other parameters monitored for plants tested previously, e.g., opacity, were not measured in Plant No. 6. Due to defective meters or lack of measurement capacity, coal usage was estimated by measuring the depth change in the coal feed bunkers one day during a 6-hr period when new coal was not being loaded into the bunkers. All other information was obtained from meters in the control room.

Electrostatic precipitator operating conditions during the test period are summarized in Table 48. Parameters observed were primary voltage (AC-v), precipitator average current (DC-amp), primary current (AC-amp), and spark rate. Values were read from meters on the ESP control units.

A summary of system changes, upsets and breakdowns is listed in Table 49. Other than a brief coal feeder breakdown on day 1, the only variations in operation were due to variations in load demand.

The results of fuels analysis for 5-day composites of coal, bottom ash, and fly ash from Plant No. 6 are shown in Table 50.

PLANT NO. 7

Table 51 shows the daily data summaries for flue gas sampling at Plant No. 7. The volumes sampled for plant background air are shown in Table 52.

Table 53 lists the process data monitored during the flue gas sampling period. Parameters observed included gross output (mw), steam flow (lb/hr), % O_2 in the flue gas (from right and left heaters), primary air heater output temperature (°F from right and left heaters), opacity, and coal loading rate (lb/hr). All information was obtained from meters in the control room.

The control meters for each of 20 ESP sections showed little variation with time. The ranges of values were as follows:

	DC-kv	DC-mA
Normal Range	25 - 40	400 - 1,500
Extremes	5 - 42	50 - 1,700

TABLE 45. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 6

Test No.	Sampling location	Sample volume		Gas composition[a]				Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Flue gas flow[b]			Isokinetic rate (%)
		dscf	dscm	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)					acfm	dscfm	dscmm	
1	A	475.20	13.46	5.7	12.5	28.3	ND[c]	372	30.49	7.9	56.05	1,440,000	832,000	23,600	101.7
	B	488.38	13.83					341	30.49	7.7	55.60				100.4
2	A	375.59	10.64	5.9	12.5	12.1	0.6	373	30.21	8.0	56.63	1,459,000	843,000	23,900	99.7
	B	395.15	11.19					336	30.21	8.0	56.47				99.8
3	A	314.65	8.91	5.0	12.6	17.9	ND	376	30.31	8.2	56.80	1,471,000	843,000	23,900	100.3
	B	329.22	9.32					344	30.31	8.3	57.27				99.6
4	A	355.55	10.07	5.6	12.8	36.4	ND	365	30.44	8.5	52.90	1,393,000	799,000	22,600	100.6
	B	277.62	7.86					343	30.44	8.8	55.05				100.3
5	A	312.71	8.86	5.5	12.9	15.1	ND	364	30.45	8.0	56.30	1,479,000	854,000	24,200	99.4
	B	337.14	9.55					338	30.45	8.4	58.37				99.7

[a] Average values for duration of test.

[b] Sum of the flow through the total outlet.

[c] ND = not detected.

TABLE 46. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 6

Test	Volume	
	dscf	dscm
1	349.65	9.90
2	346.96	9.83
3	329.39	9.33
4	322.02	9.12
5	325.78	9.23

TABLE 47. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 6

Test	Gross output (mw)	Steam flow[a] (10^6 lb/hr)	Temperature at superheater outlets (°F) A	Temperature at superheater outlets (°F) B	Excess O_2 (%)	Coal usage (tons/hr)
1 - Average	180	1.118	980	1,005	3.2	105[b]
Range	176-185	N/A	960-990	1,000-1,010	3.0-3.5	N/A
2 - Average	184	1.145	980	1,000	3.1	N/A
Range	182-186	N/A	970-990	990-1,020	2.9-3.5	N/A
3 - Average	185	1.155	970	1,005	3.3	N/A
Range	185-187	N/A	950-980	1,000-1,010	3.0-3.4	N/A
4 - Average	170	1.060	960	1,000	3.2	N/A
Range	109-185	N/A	940-990	980-1,010	2.8-3.5	N/A
5 - Average	176	1.120	960	1,000	3.2	N/A
Range	175-177	N/A	950-980	990-1,010	3.0-3.5	N/A

[a] Value is calculated from an integrator during the test period.

[b] Coal usage could only be estimated by measuring the depth change in the coal feed bunkers when new coal was not being loaded into the bunkers.

TABLE 48. SUMMARY OF ELECTROSTATIC PRECIPITATOR OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 6

Test	Primary voltage (AC-v)	Precipitator average current (DC-amp)	Primary current (AC-amp)	Spark rate (sparks/min)
1 - Unit A - Average	440	0.75	100	90
Range	430-460	0.75	100	70-100
Unit B - Average	400	0.95	124	70
Range	400-410	0.95	120-128	20-100
2 - Unit A - Average	450	0.75	100	80
Range	450-460	0.75	100	60-100
Unit B - Average	415	0.95	122	40
Range	410-420	0.95	120-126	10-60
3 - Unit A - Average	445	0.7	100	95
Range	440-450	0.7-0.8	100	90-100
Unit B - Average	415	0.9	120	80
Range	410-420	0.9	120	60-100
4 - Unit A - Average	440	0.8	95	90
Range	440-450	0.6-0.9	90-112	50-100
Unit B - Average	420	0.9	122	50
Range	400-420	0.9	120-128	10-90
5 - Unit A - Average	440	0.7	90	100
Range	430-450	0.7	90	100
Unit B - Average	420	0.9	120	35
Range	420	0.9	120	30-40

NOTE: Both units were functioning during all test runs.

TABLE 49. LOG OF SYSTEM CHANGES, UPSETS, AND BREAKDOWNS DURING FLUE GAS TESTING, PLANT NO. 6

Test Day 1	- A coal feeder was out briefly about 8 hr into the test period. The load was up slightly for the rest of the test following recovery.
Test Days 2 and 3	- Very stable operating conditions during the test period.
Test Day 4	- Variations in output load due to varying demand on Sunday.
Test Day 5	- Very stable operating conditions during the test period.

TABLE 50. PROXIMATE AND ULTIMATE ANALYSIS RESULTS FOR COAL, BOTTOM ASH, AND FLY ASH, PLANT NO. 6

	Coal	Bottom ash	Fly ash
Proximate analysis			
Reported as received			
Moisture (%)	15.97	3.70	0.00
Ash (%)	11.06	96.10	97.09
Volatile (%)	32.90	ND[a]	1.26
Fixed carbon (%)	40.07	1.06	1.65
Sulfur (%)	3.99	0.14	0.64
Heat of combustion (Btu/lb)	8,895	23	105
Dry basis			
Ash (%)	13.16	99.79	97.09
Volatile (%)	39.15	ND	1.26
Fixed carbon (%)	47.69	1.10	1.65
Sulfur (%)	4.75	0.15	0.64
Heat of combustion (Btu/lb)	10,586	24	105
A and M free Btu (Btu/lb)	12,190	11,339	3,615
Ultimate analysis			
Dry Basis			
Hydrogen (%)	4.62	0.12	0.00
Carbon (%)	61.83	0.87	0.02
Nitrogen (%)	5.76	0.00	0.00
Oxygen (%)	10.07	0.00	2.25
Total chlorine (ppm)[b]	255, 341	151, 150	276, 331

[a] ND = not detected.

[b] Duplicate determinations.

TABLE 51. DAILY DATA SUMMARIES FOR FLUE GAS SAMPLING, PLANT NO. 7

Test No.	Sampling location	Sample volume		Gas composition[a]				Stack Temperature (°F)	Molecular weight	Moisture (%)	Velocity (ft/sec)	Flue gas flow[b]			Isokinetic rate (%)
		dscf	dscm	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)					acfm	dscfm	dscmm	
1	A	360.95	10.22	3.8	14.3	13.6	ND[c]	303	30.42	8.6	46.72	1,374,000	875,000	24,800	99.3
	B	351.71	9.96					298	30.32	8.3	46.13				99.5
2	A	326.18	9.24	4.2	13.9	11.5	ND	298	30.45	8.6	42.37	1,270,000	814,000	23,000	98.6
	B	333.42	9.44					292	30.18	7.9	43.47				99.3
3	A	292.94	8.30	4.8	13.6	13.6	ND	284	30.30	7.8	36.63	1,147,000	749,000	21,200	100.0
	B	320.31	9.07					280	30.21	7.9	40.87				100.0
4	A	299.17	8.47	5.2	13.1	13.2	ND	268	30.23	7.7	33.85	1,027,000	690,000	19,600	99.6
	B	318.92	9.03					259	30.26	7.6	35.57				99.7
5	A	319.35	9.04	5.2	13.8	12.2	ND	277	30.16	8.7	36.65	1,087,000	715,000	20,300	100.6
	B	327.26	9.27					265	30.22	8.4	36.80				100.7

[a] Average values for duration of test.

[b] Sum of the flow through the total outlet.

[c] ND = not detected.

TABLE 52. SUMMARY OF PLANT BACKGROUND AIR VOLUMES, PLANT NO. 7

Test	Volume dscf	 dscm
1	466.07	13.20
2	387.58	10.98
3	383.48	10.86
4	363.33	10.29
5	360.18	10.20

TABLE 53. SUMMARY OF PLANT OPERATING CONDITIONS DURING FLUE GAS TESTING, PLANT NO. 7

Test	Gross output (Mw)	Steam flow (10^6 lb/hr)	Flue gas O_2 %		Primary air heater outlet temperature (°F)		Opacity (%)	Coal loading rate (lb/hr)
			Right	Left	Right	Left		
1 - Average	360	2.4	2.2	4.0	302	306	9	280,000
Range	343-370	2.2-2.4	2.0-2.2	3.8-4.1	294-305	298-311	5-13	260,000-288,000
2 - Average	340	2.2	2.5	4.0	303	303	10	260,000
Range	220-376	1.4-2.4	2.0-5.2	2.8-5.5	268-308	264-313	9-11	224,000-294,000
3 - Average	290	1.8	3.5	4.6	289	286	10	220,000
Range	216-368	1.3-2.4	2.8-4.8	3.0-6.0	261-317	262-314	8-12	188,000-254,000
4 - Average	250	1.5	3.9	5.6	260	270	9	190,000
Range	216-313	1.3-2.0	3.0-4.2	4.6-6.0	250-271	252-280	9-10	164,000-214,000
5 - Average	260	1.8	2.9	5.0	262	268	10	196,000
Range	215-370	1.3-2.4	2.2-4.2	3.8-6.0	252-305	254-319	9-15	160,000-278,000

Most of the time during all test runs, the spark rate was zero on 19 section panels, and was pegging the meter (> 250 sparks per minute) on the other section meters. However, around 1200 to 1500 hr daily, as many as six additional panel meters indicated spark rates between 10 to 250 sparks per minute before returning to zero later in the day.

It is likely that the ESP was working due to the almost constant opacity level of 10% (which agreed with casual visual observation). Possibly, the panel spark meters were not properly calibrated or suffered from another malfunction. However, the difficulties in collecting fly ash samples might indicate an actual malfunction of the ESP.

A summary of system changes, upsets and breakdowns is listed in Table 54. Other than a brief coal mill outage during Run 5, all variations in operation were due to variations in load demand.

TABLE 54. LOG OF SYSTEM CHANGES, UPSETS, AND BREAKDOWNS DURING FLUE GAS TESTING, PLANT NO. 7

Test Day 1	- Very stable operating conditions during the entire test period.
Test Day 2	- Stable operating conditions for about 7 hr followed by reduction in load due to reduced demand.
Test Days 3 and 4	- Constant variation in operations due to variable load demand.
Test Day 5	- Very low load for 8 hr followed by high load level for the final 4 hr. There was a very brief drop in load due to a coal mill outage.

The results of fuels analysis on 5-day composites of coal, bottom ash, fly ash, and economizer ash from Plant No. 7 are shown in Table 55.

TABLE 55. PROXIMATE AND ULTIMATE ANALYSES FOR COAL, BOTTOM ASH, FLY ASH, AND ECONOMIZER ASH FROM PLANT NO. 7

	Coal	Bottom ash	Fly ash	Economizer ash
Proximate analysis				
Reported as received				
Moisture (%)	6.27	12.07	0.02	0.02
Ash (%)	9.32	61.74	97.74	98.44
Volatile (%)	28.43	13.39	1.36	0.73
Fixed carbon (%)	55.98	12.80	0.88	0.81
Sulfur (%)	1.99	0.90	0.39	0.17
Heat of combustion (Btu/lb)	12,546	3,751	44	53
Dry basis				
Ash (%)	9.95	70.22	97.76	98.46
Volatile (%)	30.33	15.23	1.36	0.73
Fixed carbon (%)	59.73	14.55	0.88	0.81
Sulfur (%)	2.12	1.02	0.39	0.17
Heat of combustion (Btu/lb)	13,385	4,266	44	53
A and M free Btu (Btu/lb)	14,863	14,322	1,952	3,468
Ultimate analysis				
Dry basis				
Hydrogen (%)	4.97	1.81	0.07	0.04
Carbon (%)	72.24	26.77	1.21	1.27
Nitrogen (%)	0.82	0.59	0.00	0.11
Oxygen (%)	9.90	0.00	0.58	0.06
Total chlorine (ppm)[a]	700 ± 290	700, 900	100, 100	100, 100

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[a] Mean ± standard deviation for four determinations on coal. Duplicate determinations for ashes.

SECTION 8

ANALYTICAL RESULTS

The analytical results generated from this program include data from HRGC/Hall-FID screening, scanning HRGC/MS for target compounds, and HRGC/MS-SIM analysis of the sample extracts for PCBs, PCDDs and PCDFs.

HRGC/HALL-FID SCREEN

The HRGC/Hall-FID screening procedure used for Plant Nos. 1 to 4, was useful in identifying the sample extracts that contained halogenated organic compounds. The Hall chromatograms for grab and plant background air samples from Plant Nos. 1 to 4 and the flue gas samples from Plant No. 3 did not contain significant peaks other than the chlorinated surrogate spiking compounds. Halogenated compounds were indicated in flue gas samples from Plant Nos. 1, 2, and 4. The Hall chromatograms for the five flue gas samples from each plant were quite similar. Figure 35 shows the Hall chromatograms for flue gas extracts from Plant No. 1.

SCANNING HRGC/MS ANALYSIS

The results for the target PAH and phthalate compounds identified in the flue gas, fly ash, bottom ash, economizer ash, coal, and background air samples from the seven coal-fired power plants are shown in Tables 56to 61. These data and all other analytical results reported in this document are presented without correction for recoveries. The levels of extractable organics from samples other than flue gas and coal were low. Most of the target compounds determined in the ash and background air samples were present at levels near the detection limits. No significant levels of the target compounds were identified in the water samples.

HRGC/MS-SIM ANALYSIS

PCBs

The concentrations of PCB isomers identified in flue gas samples from the seven coal-fired power plants are shown in Table 62. PCBs were identified in flue gases from all plants. However, the concentrations found in samples from Plant No. 3 were frequently at or near the method detection limit. Although the mean total PCB concentrations varied 0.01 to 1.8 µg/dscm, the distributions of PCB isomers identified in flue gases from all plants were similar. The isomer distributions were also similar to that found in the pilot study for flue gases from a utility boiler plant co-fired with coal and a refuse-derived fuel.[2] The similarity of isomer distribution for flue gas samples from seven plants is illustrated by Figure 36. The PCBs were comprised primarily of penta- and hexachlorobiphenyls with lesser contribution from tetra- and heptachlorobiphenyls.

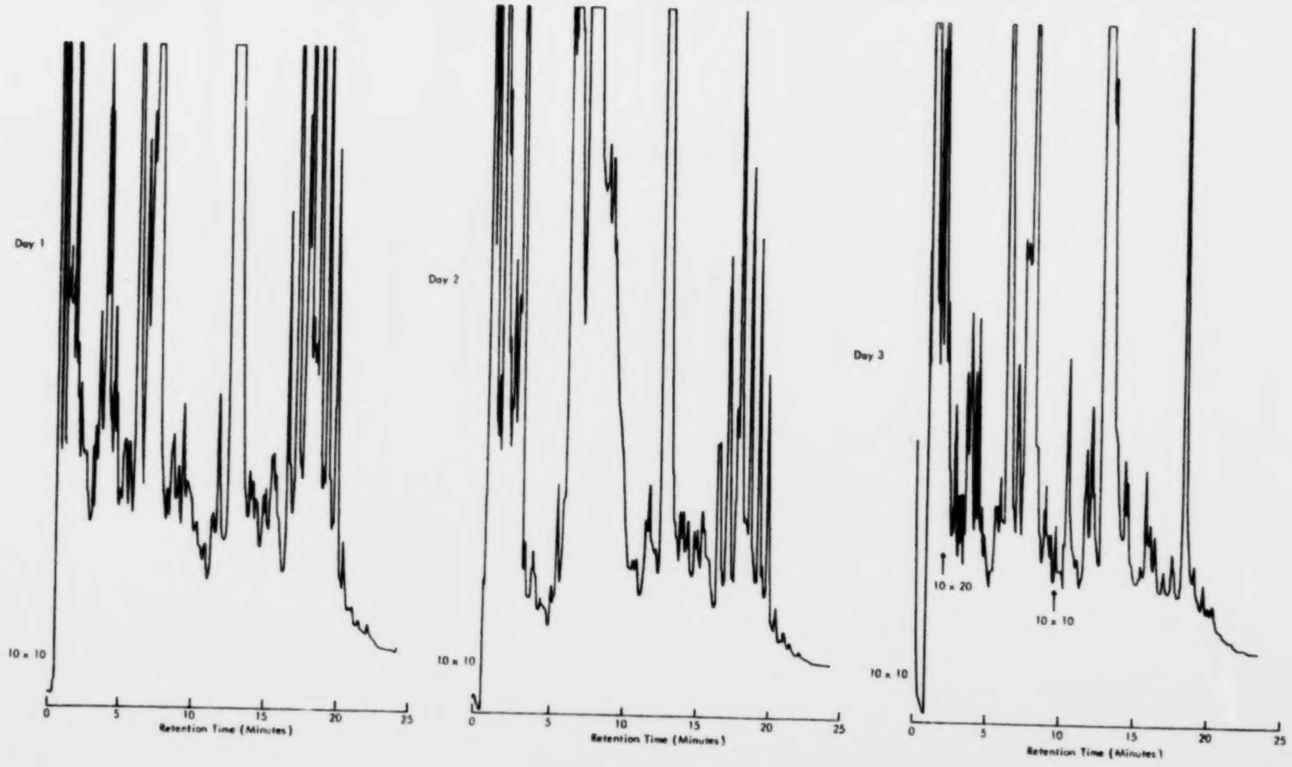

Figure 35. HRGC/Hall chromatograms of the flue gas extracts for sampling days 1-5, Plant No. 1

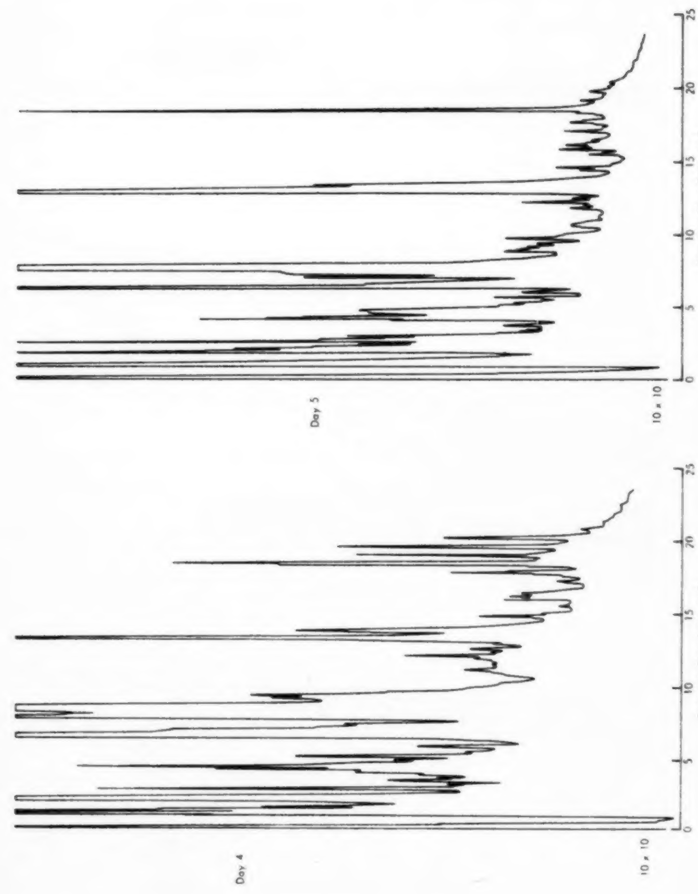

Figure 35 (concluded)

TABLE 56. TARGET COMPOUNDS IDENTIFIED IN FLUE GAS SAMPLES FROM THE SEVEN COAL-FIRED POWER PLANTS

Compound	Sampling day	Concentration (μg/dscm) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Naphthalene	1	0.37	0.57		0.43	1.2	1.0	0.48
	2	0.28		0.10	0.51	1.1	0.45	0.14
	3	0.32	1.7	0.53	1.5	0.86	1.3	0.57
	4	0.17	3.8	1.4	2.0	2.2	6.0	0.44
	5	0.34	2.5	0.33	0.78	0.83	1.1	0.65
Acenaphthylene	1							
	2							
	3			0.32				
	4							
	5	0.66						
Acenaphthene	1							
	2		tr[a]					
	3							
	4		54					
	5							
Fluorene	1	0.018						
	2	0.015			tr			
	3		0.67		0.033			0.012
	4				0.070			
	5							
Phenanthrene	1	0.21	0.42	0.06	0.071		0.95	0.045
	2	0.22			0.083		0.056	0.0064
	3		7.8		0.14		0.12	0.078
	4	0.14	1.4	0.10	0.24		0.13	0.037
	5	0.33	0.26	0.07	0.21		0.26	0.072

(continued)

TABLE 56 (continued)

Compound	Sampling day	Concentration (μg/dscm) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Fluoranthene	1	0.088						
	2	0.044						
	3		1.15					
	4	0.044			0.088			
	5				0.058			
Pyrene	1	0.057						
	2	0.024						
	3		0.32					
	4							
	5							
Chrysene	1	0.031						
	2			tr			0.070	
	3		0.75		0.048			
	4		0.14	tr	0.12	0.007		
	5			tr	0.18		0.045	
Benzo[a]pyrene	1							
	2	0.006						
	3							
	4							
	5							
Dimethylphthalate	1	0.15						
	2	0.13					0.54	0.060
	3							
	4	0.071	tr					
	5							

(continued)

TABLE 56 (continued)

Compound	Sampling day	Concentration (µg/dscm)						
		Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Diethylphthalate	1	6.0	8.7	0.42				
	2	4.1		2.3	0.79			
	3	1.9	6.5		5.0			
	4	5.8	6.8		12.3			
	5	10.5	4.1	0.49	11.7			
Di-n-butylphthalate	1	9.1	28.3					
	2	4.0		0.10	1.7			
	3	0.98	41.6					
	4	3.1	2.2					
	5	6.7	1.8					
Butyl benzylphthalate	1	1.1		0.35				
	2	0.64		0.29	0.45			
	3		4.0	tr	0.50			
	4	0.44			0.64			
	5	1.8	1.3	0.46	tr			
Bis(2-ethylhexyl)phthalate	1	12.3	5.0	2.7		21	34	0.53
	2	9.1		5.2		3.4	0.93	0.82
	3			25	15.3	9.2	11	1.4
	4	13.5		24	3.4	30	8.3	6.7
	5	7.4		6.8	31.2	8.6	0.55	18
Di-n-octylphthalate	1	1.1		0.93	0.63	2.0		
	2	4.9			0.31			
	3	0.23			0.54	0.50		
	4	2.5			1.2			
	5	1.7						

a tr = ≦ 0.025 µg/dscm.

TABLE 57. TARGET COMPOUNDS IDENTIFIED IN FLY ASH SAMPLES FROM THE SEVEN COAL-FIRED POWER PLANTS

Compound	Sampling day[a]	Concentration (ng/g)						
		Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Naphthalene								
	1			6.5	10			
	2			10	30			
	3		15	18				
	4		10	23				
	5		10					
Phenanthrene								
	1			4.3	15			
	2			6.0	10			
	3			2.3				
	4							
	5							
Chrysene								
	1						4.6	0.80
	2							
	3							
	4							
	5							
Dimethylphthalate								
	1					10.7		
	2							
	3		10					
	4		5.0					
	5		7.5					
Diethylphthalate								
	1			22	10	40		36
	2			14	30			22
	3			14				
	4			13				
	5							

(continued)

TABLE 57 (continued)

Compound	Sampling day	Concentration (ng/g) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Di-n-butylphthalate	1		120	21	10			
	2		28	30	20			
	3		78					
	4			11				
	5		18	29				
Butyl benzylphthalate	1			8.0	15		15	
	2			22	45		230	
	3		15	7.3				
	4		13	3.5				
	5		15	14				
Bis(2-ethylhexyl)phthalate	1	38		36	160	2,800	1,100	
	2	48	30	190	230	620		
	3	20	73	36				
	4	15	48	18				
	5	25	78	46				
Di-n-octylphthalate	1					390		
	2							
	3							
	4							
	5							

a Results for duplicate 5-day plant composites from Plant Nos. 4-7 are listed on days 1 and 2.

TABLE 58. TARGET COMPOUNDS IDENTIFIED IN BOTTOM ASH SAMPLES FROM THE SEVEN COAL-FIRED POWER PLANTS

Compound	Sampling day[a]	Concentration (ng/g) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Naphthalane	1	65		8.3	21	80		220
	2	18		39	1	27		210
	3	20		28				
	4	40		55				
	5	13		7.8				
Acenaphthylene	1					12		
	2					5.1		
	3							
	4							
	5							
Fluorene	1				1.5	4.4		
	2							
	3							8.7
	4							
	5							
Phenanthrene	1			2.5	12	33		63
	2			11		11		65
	3			14				
	4			33				
	5			2.0				
Fluoranthene	1				2.0	14		8.2
	2					5.9		
	3							
	4							
	5							

(continued)

TABLE 58 (continued)

Compound	Sampling day	Concentration (ng/g) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Pyrene	1				1.5	11		7.2
	2					4.2		
	3							
	4							
	5							
Chrysene	1				9.5	7.8		16
	2							16
	3			7.5				
	4			18				
	5							
Benzo[a]pyrene	1							3.9
	2							
	3			1.5				
	4			11				
	5							
Dibenzo[a,h]anthracene	1							
	2							
	3		10					
	4			3.5				
	5							
Benzo[g,h,i]perylene	1							
	2							
	3							
	4			3.1				
	5							

(continued)

TABLE 58 (continued)

Compound	Sampling day	Concentration (ng/g) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Diethylphthalate	1			24	4.5			
	2			9.0	5.5			
	3			10				
	4			3.0				
	5			9.0				
Di-n-butylphthalate	1	88			7.0			
	2	55			5.0			
	3			6.8				
	4	73	53	11				
	5	43						
Butyl benzylphthalate	1			6.0			26	
	2			1.8	13		480	
	3			3.3				
	4		15	5.8				
	5		13	3.3				
Bis(2-ethylhexyl)phthalate	1	88		47	12		560	
	2	73	43	37	7		250	
	3	70	18	21				
	4	63	33	49				
	5	60	20	26				

a Results for duplicate 5-day plant composites from Plant Nos. 4-7 are listed as days 1 and 2.

TABLE 59. TARGET COMPOUNDS IDENTIFIED IN ECONOMIZER ASH SAMPLES FROM PLANTS NOS. 3 AND 7

Compound	Sampling day[a]	Concentration (ng/g)	
		Plant No. 3	Plant No. 7
Naphthalene	1	8.3	1.4
	2		1.2
	3		
	4		
	5		
Acenaphthene	1		8.7
	2		11
	3		
	4		
	5		
Phenanthrene	1	1.3	
	2		
	3	4.0	
	4		
	4		
Dimethylphthalate	1		
	2		
	3		
	4	1.8	
	5		
Diethylphthalate	1	5.5	
	2		
	3		
	4		
	5		
Di-n-butyl phthalate	1	20	
	2	7.8	
	3		
	4	17	
	5		
Butyl benzylphthalate	1		270
	2		
	3		
	4		
	5		
Bis(2-ethylhexyl)-phthalate	1	20	
	2	26	
	3	40	
	4	31	
	5	20	

[a] Results for duplicate 5-day plant composites from Plant No. 7 are listed as days 1 and 2.

TABLE 60. TARGET COMPOUNDS IDENTIFIED IN COAL SAMPLES FROM THE SEVEN COAL-FIRED POWER PLANTS

Compound	Sampling day[a]	Concentration (μg/g)						
		Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Naphthalene	1		0.61	2.7		1.9	0.11	3.5
	2	0.06	0.30	1.6			0.072	2.7
	3		0.38	1.7				
	4		0.33	2.5				
	5		0.37	1.7				
Acenaphthylene	1		0.074	0.16			0.029	0.025
	2			0.07				0.098
	3			0.23				
	4			0.18				
	5			0.11				
Acenaphthene	1		0.020				0.46	0.061
	2		0.022				0.25	
	3		0.017					
	4							
	5			0.01				
Fluorene	1		0.055	0.095	0.16	0.12	0.72	0.18
	2		0.038	0.055	0.53		0.41	0.15
	3		0.023	0.11				
	4	0.019	0.023	0.09				
	5		0.016	0.06				
Phenanthrene	1		0.35	0.82	1.5	1.0	3.2	1.2
	2	0.10	0.32	0.45	3.2		2.5	1.0
	3	0.053	0.20	0.65				
	4	0.25	0.20	0.76				
	5	0.33	0.14	0.55				

(continued)

TABLE 60 (continued)

Compound	Sampling day	Concentration (μg/g) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Pyrene	1	0.10	0.11	0.13		0.20	0.64	0.20
	2	0.20	0.082	0.07			0.50	0.16
	3	0.16	0.059	0.15				
	4	0.19	0.056	0.11				
	5	0.054	0.033	0.10				
Chrysene	1		0.19	0.19	0.35		7.6	0.51
	2	0.034	0.18	0.15	0.36		0.53	0.55
	3		0.078	0.18				
	4	0.040	0.086	0.23				
	5		0.055	0.16				
Benzo[a]pyrene	1	0.20	0.091	0.12			0.70	0.85
	2	0.19	0.088	0.06	0.28		0.080	0.70
	3	0.17	0.048	0.095				
	4	0.40	0.029	0.070				
	5	0.54	0.027	0.08				
Dibenz[a,h]anthracene	1		0.015					
	2		0.020	0.02			0.009	
	3		0.013					
	4	0.057		0.02				
	5							
Benzo[g,h,i]perylene	1		0.086	0.21			0.56	0.062
	2		0.10	0.07			0.066	0.053
	3		0.071	0.16				
	4	0.11	0.061	0.21				
	5			0.13				

(continued)

TABLE 60 (continued)

Compound	Sampling day	Concentration (μg/g)						
		Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Fluoranthene	1			0.12		0.065	0.60	0.22
	2						0.31	0.19
	3			0.13				
	4			0.11				
	5			0.05				
Benzofluoranthene	1						0.24	0.10
	2						0.096	0.086
	3							
	4							
	5							
Butyl benzylphthalate	1					0.12		
	2							
	3							
	4							
	5							
Bis(2-ethylhexyl)phthalate	1					0.58	0.75	
	2						0.23	
	3							
	4							
	5							

[a] Results for duplicate 5-day plant composites from Plant Nos. 4-7 are listed as days 1 and 2.

TABLE 61. TARGET COMPOUNDS IDENTIFIED IN BACKGROUND AIR SAMPLES FROM THE SEVEN COAL-FIRED POWER PLANTS

Compound	Sampling day	Concentration (ng/dscm)						
		Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4[a]	Plant No. 5	Plant No. 6	Plant No. 7
Naphthalene	1	1,300	1,100	1,000				1,000
	2	1,200	2,800	2,200				1,600
	3	1,800	2,100					1,200
	4	1,700	2,800					
	5	2,000	2,100	2,600		690		
Acenaphthene	1					78	4.8	31
	2						8.6	
	3						11	27
	4							
	5					20		
Fluorene	1							
	2							
	3						15	34
	4							
	5						59	
Phenanthrene	1							96
	2			190				
	3							120
	4							
	5			490				
Fluoranthene	1							18
	2							27
	3						18	
	4						180	
	5							
Pyrene	1							
	2							
	3							
	4						16	
	5			170				

(continued)

TABLE 61 (continued)

Compound	Sampling day	Concentration (ng/dscm) Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4[a]	Plant No. 5	Plant No. 6	Plant No. 7
Chrysene	1					18		8.6
	2							
	3							
	4							
	5							
Diethylphthalate	1	450	350					
	2	370	480					
	3	550	720					
	4		960					
	5	580	970	2,400				
Di-n-butylphthalate	1	360	120					
	2	390	260					
	3	480	140					
	4	940						
	5	550						
Butyl benzylphthalate	1	91						
	2	91						
	3							
	4						710	
	5	120						
Bis(2-ethylhexyl)phthalate	1	380	210	2,500				
	2	430	310	3,000				
	3	320	250					
	4	390	270					
	5	1,300	1,500	3,600				

[a] Extract aliquots prepared for scanning HRGC/MS were lost.

TABLE 62. POLYCHLORINATED BIPHENYL ISOMERS IDENTIFIED IN FLUE GAS OUTLET SAMPLES

		Concentration (μg/dscm)						
Compound	Sampling day	Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Tetrachlorobiphenyl	1	0.15	0.17		0.59	tr[a]	tr	tr
	2	0.11	0.10		0.20	tr	tr	
	3	0.01	0.22		0.28	tr		tr
	4	0.13	0.05		0.28	tr		tr
	5	0.08	0.002		0.06	tr	tr	tr
Pentachlorobiphenyl	1	1.86		0.015	1.60	0.013	0.26	0.009
	2	1.15	0.32	0.003	0.32	0.006	0.095	
	3	0.11	0.08	tr	0.35	0.009	0.010	
	4	1.31	0.60	tr	0.15	0.009	0.032	0.010
	5	0.29	0.06	tr		tr	0.18	0.046
Hexachlorobiphenyl	1	0.93	0.01	0.033	1.09	0.007	0.12	0.005
	2	0.58	0.15	tr	0.15	0.002	0.047	
	3	0.06	0.02	0.0012	0.26	0.005	0.004	
	4	0.74	0.32	tr	0.48	0.003	0.015	0.004
	5	0.11	0.04	tr	0.11	tr	0.18	0.048
Heptachlorobiphenyl	1	0.18			1.13		0.045	
	2	0.14	0.06		0.13		0.028	
	3	0.02			0.54			
	4	0.25	0.07		0.87		0.013	
	5	0.06	0.002		0.37		0.076	
Octachlorobiphenyl	1	0.004			0.17		0.002	
	2	0.003						
	3							
	4							
	5						0.002	

(continued)

TABLE 62 (continued)

Compound	Sampling day	Concentration (μg/dscm)						
		Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Total chlorobiphenyl	1	3.1	0.18	0.048	4.6	0.020	0.43	0.014
	2	2.0	0.63	0.0026	0.8	0.008	0.17	≦ 0.002
	3	0.2	0.32	0.0012	1.4	0.014	0.014	≦ 0.002
	4	2.4	1.04	tr	1.8	0.012	0.074	0.014
	5	0.5	0.10	tr	0.5	≦ 0.004	0.44	0.094
Mean		1.6	0.45	0.010	1.8	0.012	0.22	0.025
Standard deviation		1.3	0.38	0.021	1.6	0.006	0.20	0.039

a tr = ≦ 0.00005 μg/dscm.

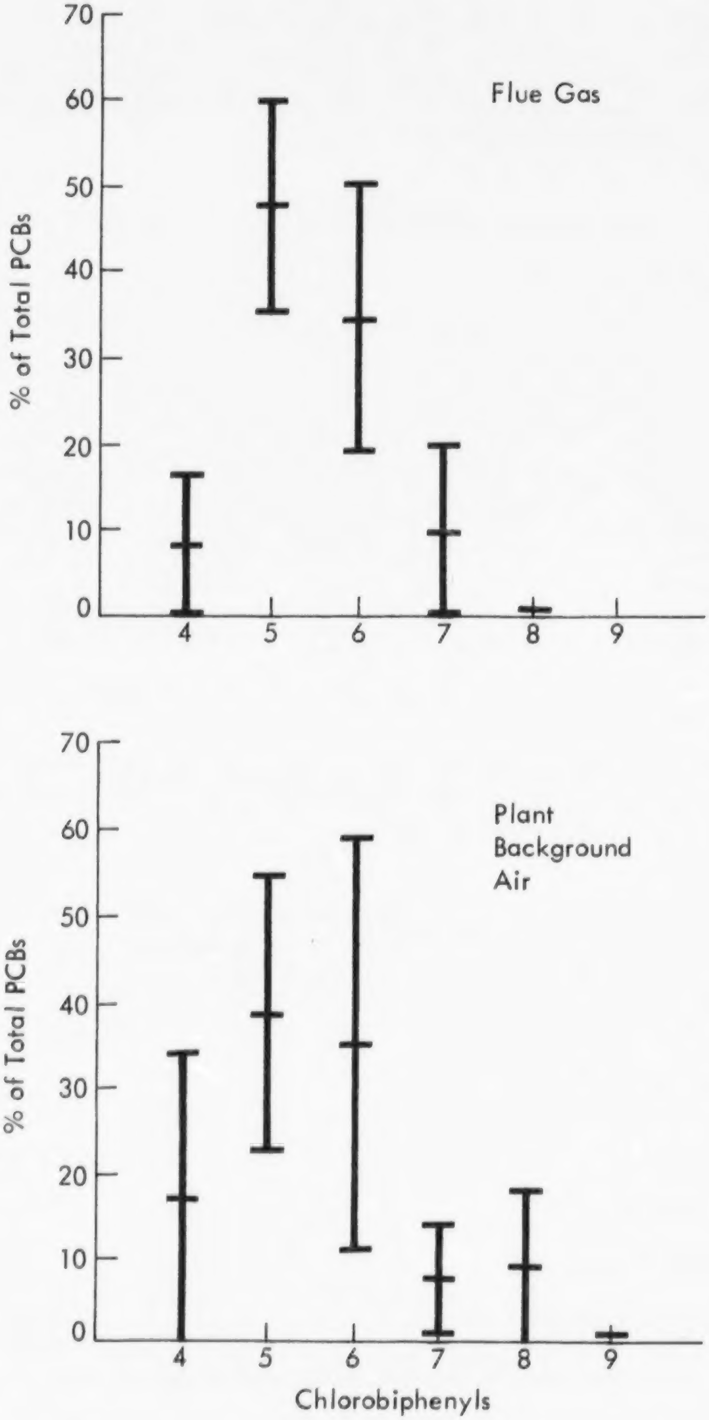

Figure 36. Average distribution (mean ± standard deviation) of chlorobiphenyls in coal-fired power plant flue gas and plant background air.

The concentrations of PCB isomers identified in plant background air samples are shown in Table 63. These results are for analyses of 5-day composite samples. PCBs were not identified in the composite sample from Plant No. 3. The PCB isomer distributions observed for these samples are similar to those for the flue gas samples.

TABLE 63. PCB ISOMERS IDENTIFIED IN PLANT BACKGROUND AIR SAMPLES

	Concentration (μg/dscm)					
Compound	Plant No. 1	Plant No. 2	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Tetrachlorobiphenyl	0.081	0.096				
Pentachlorobiphenyl	0.12	0.12	0.15	0.004	0.001	0.001
Hexachlorobiphenyl	0.022	0.022	0.37	0.002	0.002	0.002
Heptachlorobiphenyl	0.009	0.007	0.17			
Octachlorobiphenyl			0.32			
Nonachlorobiphenyl			0.027			
Decachlorobiphenyl				0.001	0.0004	
Total chlorobiphenyl	0.23	0.25	1.04	0.007	0.0034	0.003

PCBs were not identified in any of the grab samples from the four coal-fired power plants. Table 64 shows the method detection limits for PCBs in the grab samples and plant background air samples.

TABLE 64. METHOD DETECTION LIMITS FOR PCB ISOMERS IN GRAB SAMPLES

Sample type	Detection limit
Bottom ash[a]	1 ng/g
Fly ash[a]	1 ng/g
Economizer ash[a]	1 ng/g
Aqueous samples[b]	20 ng/ℓ
Plant background air[c]	2 ng/dscm

a Five-day composite equivalent to a 100-g sample.

b Five-day composite equivalent to a 5-ℓ sample.

c Five-day composite equivalent to 50 dscm.

PCDDs and PCDFs

PCDD and PCDF isomers were not identified in any sample from the seven coal-fired power plants. All samples were analyzed using 5-day composites to maximize the method sensitivity. The method detection limits for each sample type are shown in Table 65. Figure 37 shows the SIM ion plots for a 2.5 pg injection of 1,2,3,4-TCDD.

TABLE 65. METHOD DETECTION LIMITS FOR PCDDs AND PCDFs FOR 5-DAY COMPOSITE FLUE GAS AND GRAB SAMPLES

Sample type	Units	Dioxin and furan isomers			
		Cl_1 - Cl_3	Cl_4	Cl_5, Cl_6	Cl_7, Cl_8
Flue gas[a]	pg/dscm	250	100	500	700
Bottom ash[b]	pg/g	25	10	50	70
Fly ash[b]	pg/g	25	10	50	70
Economizer ash[b]	pg/g	25	10	50	70
Plant background air[c]	pg/dscm	50	20	100	140
Aqueous samples[d]	pg/L	500	200	1,000	1,400

[a] All flue gas samples were diluted 1:10 for HRGC/MS-SIM analysis. The 5-day composite was calculated as equivalent to 10 dscm.

[b] The 5-day composite is equivalent to a 100-g sample.

[c] The 5-day composite is equivalent to a 50-dscm sample.

[d] The 5-day composite is equivalent to a 5-ℓ sample.

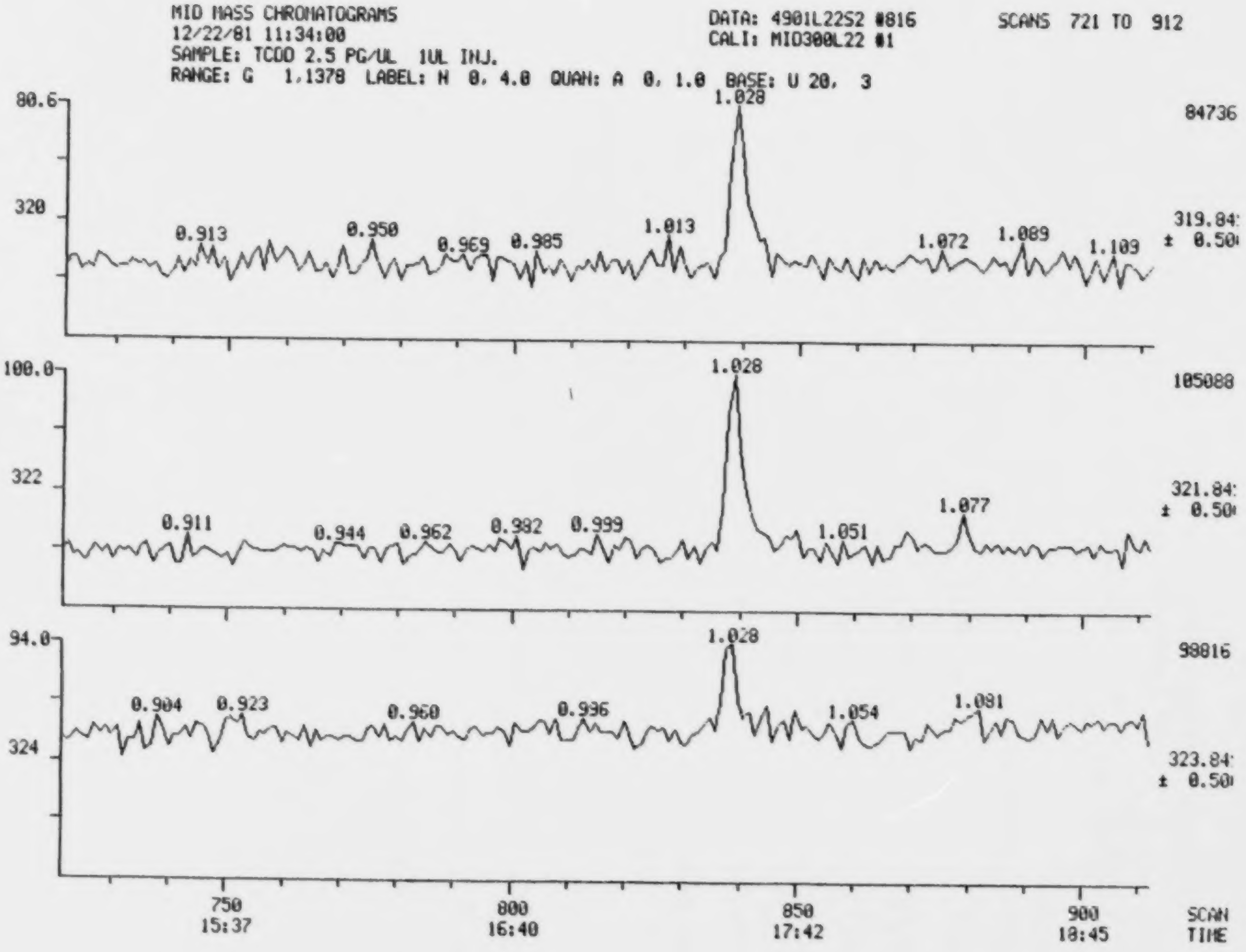

Figure 37. SIM response to a 2.5 pg injection of 1,2,3,4-TCDD.

SECTION 9

ANALYTICAL QUALITY ASSURANCE RESULTS

The primary indicators of the performance of the analytical procedures for this study were the recoveries of surrogate spiking compounds. These results are presented and discussed in this section. Another key aspect of the quality assurance procedures used in this study was the performance of the fused silica capillary columns used for HRGC and HRGC/MS analyses. This section also discusses the column performance checks and presents the results of the development of a performance evaluation solution used for HRGC/Hall-FID.

SURROGATE COMPOUND RECOVERIES

The surrogate compound recoveries for samples from Plant No. 1 are shown in Tables 66 to 73. These tables also show the means and standard deviations for recoveries from samples from the five sampling days. The ash, water, and coal samples were analyzed in duplicate. The average percent deviation for the duplicate determinations are shown in the appropriate tables. Table 74 is a summary of the average recoveries for the Plant No. 1 samples. The recoveries and standard deviations generally indicate that the precision and accuracy were good for all compounds except pentachlorophenol-$^{13}C_6$. Pentachlorophenol (PCP) is very polar and acidic, more polar than the target analytes. This characteristic is manifested in a gas chromatographic peak shape for PCP that is generally broad and very susceptible to changes in the activity of the column. Hence, the recovery of pentachlorophenol-$^{13}C_6$ provides an indication of the maximum apparent losses due to adsorption on the fused silica capillary column.

The average percent deviations for duplicate determinations were generally good. Excluding pentachlorophenol-$^{13}C_6$, the average value for all compounds in all sample types was 18%.

The surrogate recoveries for the flue gas samples are generally lower than for all other sample types. This is likely caused by the high levels of extractable materials in the flue gas extracts. Even after cleanup on silica gel, the flue gas extracts required dilution prior to scanning HRGC/MS analysis. The dilution reduced the maximum concentrations of the surrogate compounds to just above their detection limits so that accurate and precise determination was difficult.

TABLE 66. SURROGATE COMPOUND RECOVERIES IN FLUE GAS SAMPLES, PLANT NO. 1

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	54	16	11	18	46
2	56	30	6	22	100
3	19	14	7	10	82
4	9	14	28	13	97
5	35	32	74	30	70
Mean	35	21	25	19	79
Standard deviation	21	9	29	4	22

TABLE 67. SURROGATE COMPOUND RECOVERIES IN BOTTOM ASH SAMPLES, PLANT NO. 1

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	60, 67	71, 74	60, 77	120, 150	68, 81
2	55, 52	68, 66	58, 48	140, 110	57, 42
3	53	60	57	76	8
4	46, 39	72, 68	45, 27	65, 85	70, 66
5	47, 44	89, 53	59, 50	61, 70	62, 44
Mean	52	68	54	95	51
Standard deviation	8	5	12	32	26
Average % deviation for duplicates	5	8	12	12	10

TABLE 68. SURROGATE COMPOUND RECOVERIES IN FLY ASH SAMPLES, PLANT NO. 1

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	30, 31	88, 123	55, 69	98, 210	230, 570
2	27, 27	73, 101	29, 39	79, 100	210, 180
3	32, 31	83, 32	33, 29	46, 64	82, 180
4	26, 27	100, 110	32, 52	98, 110	120, 180
5	46, 47	43, 43	33, 40	50, 47	44, 29
Mean	32	80	41	90	183
Standard deviation	8	28	12	42	135
Average % deviation for duplicates	1	16	13	18	30

TABLE 69. SURROGATE COMPOUND RECOVERIES IN COAL SAMPLES FROM PLANT NO. 1

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	50	59	42	48	25
2	100	110	83	71	ND[a]
3	76, 100	54, 130	46, 57	39, 98	29, 76
4	100, 130	130, 130	67, 74	97, 88	89, 95
5	130	110	78	99	94
Mean	98	100	65	76	65
Standard deviation	31	27	18	20	31
Average % deviation for duplicates	11	17	7	21	18

[a] ND = Not determined.

TABLE 70. SURROGATE COMPOUND RECOVERIES IN PLANT BACKGROUND AIR SAMPLES, PLANT NO. 1

	% Recovery				
Day	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	36	99	32	70	2
2	30	21	17	29	2
3	50	79	68	98	1
4	48	78	60	75	2
5	51	82	81	110	0
Mean	43	72	52	76	1
Standard deviation	9	30	26	31	1

TABLE 71. SURROGATE COMPOUND RECOVERIES IN RAW WATER SAMPLES, PLANT NO. 1

	% Recovery				
Day	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
2	39	55	93	110	7
3	25	45	32	68	5
4	64, 58	90, 82	130	140, 140	4, 2
5	55, 37	110, 71	62, 100	96, 130	9, 79
Mean	43	69	84	108	15
Standard deviation	15	22	40	30	20
Average % deviation for duplicates	11	13	—	7	80

TABLE 72. SURROGATE COMPOUND RECOVERIES IN BOTTOM ASH QUENCH EFFLUENT WATER SAMPLES, PLANT NO. 1

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	48, 48	53, 76	84, 76	110, 100	54, 33
2	16, 16	30, 33	26, 20	26, 35	50, 0
3	11, 24	19, 41	15, 38	17, 38	0, 0
4	1, 1	61, 60	11, 7	60, 69	48, 22
5	33, 73	41, 89	35, 70	54, 97	15, 41
Mean	27	50	38	61	26
Standard deviation	22	18	28	32	16
Average % deviation for duplicates	20	11	20	15	47

TABLE 73. SURROGATE COMPOUND RECOVERIES IN BOTTOM ASH QUENCH INFLUENT WATER SAMPLES, PLANT NO. 1

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	37	50	50	55	0
2	1, 36	51, 46	12, 40	51, 65	0, 0
3	48, 27	88, 53	87, 60	110, 86	0, 4
4	1, 29	50, 55	3, 61	53, 80	0, 0
5	48, 70	88, 94	100, 100	120, 130	0, 2
Mean	33	63	56	80	1
Standard deviation	18	18	31	29	1
Average % deviation for duplicates	40	10	25	11	

TABLE 74. AVERAGE RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 1

Sample type	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
Flue gas	35 ± 21[a]	21 ± 9	25 ± 29	19 ± 4	79 ± 22
Bottom ash	52 ± 8	68 ± 5	54 ± 12	95 ± 32	61 ± 12
Fly ash	32 ± 8	80 ± 28	41 ± 12	90 ± 42	183 ± 135
Coal	98 ± 31	100 ± 27	65 ± 18	76 ± 20	65 ± 31
Plant background air	43 ± 9	72 ± 30	52 ± 26	76 ± 31	1 ± 1
Quench influent	33 ± 18	63 ± 18	56 ± 31	80 ± 29	1 ± 1
Quench effluent	27 ± 22	50 ± 18	38 ± 28	61 ± 15	26 ± 16

[a] Mean ± standard deviation.

The surrogate compound recoveries for samples from Plant Nos. 2-7 are shown in Tables 75 to 100. The plant data summaries are shown in Tables 81, 89, 91, 94, 97, and 100 for Plant Nos. 2, 3, 4, 5, 6, and 7, respectively.

The recoveries and recovery levels for samples from Plant Nos. 2 and 3 are very similar to those discussed for Plant No. 1. The average percent deviation for duplicate analyses of grab samples for Plant Nos. 2 and 3 are both 16% (excluding pentachlorophenol-$^{13}C_6$). The recoveries for economizer ash from Plant No. 3 were consistently lower than those for bottom ash and fly ash from the same plant. As shown in Table 32 (Section 7), the economizer ash has a much higher fixed carbon content and is lower in volatiles than bottom ash or fly ash. Hence, the economizer ash may have adsorption properties similar to that of activated charcoal.

Since grab samples from Plant Nos. 4 to 7 were analyzed as plant composites, surrogate recoveries for those samples are included only in the plant summary tables. Separate tables show recovery results for daily flue gas samples from each of Plant Nos. 4 to 7 and for daily plant background air samples from each of Plant Nos. 5 to 7.

The mean recoveries of each surrogate compound for the seven plants are also illustrated by bar plots for each sample shown in Figures 38 to 45. Most of these plots show considerable differences in surrogate recoveries from plant to plant, likely due, at least in part, to differences in the characters of samples from the different plants. One of the most conspicuous observations from the bar plots are low recoveries of pentachlorophenol-$^{13}C_6$ from water samples. Since the water samples were extracted without adjustment to acidic pH, much of the pentachlorophenol spike may have remained ionized in the aqueous solution.

The surrogate recovery data for samples from all plants are summarized in Table 101. As noted previously, the recoveries observed for the surrogate compounds are generally lower for flue gas samples. The surrogate compounds were spiked into the three components of the flue gas samples according to the schedule described in Section 6. Table 102 summarizes the surrogate recovery data for all flue gas samples by the sample component spiked. These results indicate that the recoveries were independent of the train component spiked.

BLANK SAMPLE RESULTS

Solvent blanks, container blanks, and flue gas train component blanks from Plant Nos. 1 to 4 were screened using HRGC/Hall-FID. All flue gas train blanks, i.e., two complete trains for each plant, from all plants and all other blank samples from Plant Nos. 5 to 7 were analyzed using HRGC/MS. All flue gas blank samples were also analyzed for PCBs, PCDDs, and PCDFs by HRGC/MS-SIM. In general, only low concentrations of phthalate esters were identified. All results from sample analyses were blank corrected. Analyte identifications were reported only for concentrations greater than two times the concentrations in the corresponding blanks. No PCB, PCDD, or PCDF compounds were identified in any flue gas blank samples.

TABLE 75. SURROGATE COMPOUND RECOVERIES IN FLUE GAS SAMPLES, PLANT NO. 2

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	14	43	8	14	75
3	3	47	0	29	NS[a]
4	41	61	0	8	87
5	30	43	27	23	60
Mean	22	49	16	19	56
Standard deviation	17	9	13	9	39

[a] NS = Not spiked.

TABLE 76. SURROGATE COMPOUND RECOVERIES IN BOTTOM ASH SAMPLES, PLANT NO. 2

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	54, 56	82, 70	54, 79	110, 86	92, 71
2	49, 48	70, 69	56, 69	100, 78	73, 76
3	50, 67	64, 92	54, 94	81, 84	74, 120
4	92, 81	130, 82	110, 73	93, 130	160, 120
5	66, 71	84, 81	75	71, 65	120, 170
Mean	63	82	74	90	107
Standard deviation	15	13	11	16	33
Average % deviation for duplicates	6	25	15	22	14

TABLE 77. SURROGATE COMPOUND RECOVERIES IN FLY ASH SAMPLES, PLANT NO. 2

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	34	41	37	52	0
2	49, 79	51, 83	46, 82	66, 94	0, 0
3	48, 64	50, 64	63, 74	55, 84	2, 2
4	57, 54	64, 55	74, 52	65, 58	29, 7
5	62, 76	66, 77	62, 63	87, 103	42, 23
Mean	56	59	59	72	11
Standard deviation	13	12	13	17	14
Average % deviation for duplicates	13	13	13	13	39

TABLE 78. SURROGATE COMPOUND RECOVERIES IN COAL SAMPLES, PLANT NO. 2

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	71, 73	88, 89	230, 280	76, 87	73, 76
2	130, 70	190, 100	71, 270	110, 94	99, 100
3	35, 49	75, 74	67, 120	24, 60	36, 50
4	73, 49	73, 71	200, 110	77, 52	87, 47
5	53, 53	61, 91	100, 100	50, 50	29, 36
Mean	66	91	155	68	64
Standard deviation	22	31	65	24	27
Average % deviation for duplicates	15	14	25	13	11

TABLE 79. SURROGATE COMPOUND RECOVERIES IN PLANT BACKGROUND AIR SAMPLES, PLANT NO. 2

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	43	46	52	51	0
2	63	46	52	44	0
3	54	39	42	44	0
4	70	54	53	46	0
5	46	37	40	29	0
Mean	55	44	48	43	-
Standard deviation	11	7	6	8	

TABLE 80. SURROGATE COMPOUND RECOVERIES IN BOTTOM ASH QUENCH EFFLUENT WATER SAMPLES, PLANT NO. 2

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	67	74	64	72	7
2	51	59	72	95	11
3	78	85	84	91	24
4	60	59	52	47	23
5	61	65	53	86	16
Mean	63	68	65	78	16
Standard deviation	10	11	13	19	7

TABLE 81. AVERAGE RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 2

	% Recovery				
Sample type	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
Flue gas	22 ± 17[a]	49 ± 9	16 ± 13	19 ± 9	56 ± 39
Bottom ash	63 ± 6	82 ± 13	74 ± 11	90 ± 16	110 ± 33
Fly ash	56 ± 13	59 ± 12	59 ± 13	72 ± 17	11 ± 14
Coal	66 ± 22	91 ± 31	160 ± 65	68 ± 24	64 ± 27
Plant background air	55 ± 11	44 ± 7	48 ± 6	43 ± 8	0
Aqueous effluent	63 ± 10	68 ± 11	65 ± 13	78 ± 19	16 ± 7

[a] Mean ± standard deviation.

TABLE 82. SURROGATE COMPOUND RECOVERIES IN FLUE GAS SAMPLES, PLANT NO. 3

	% Recovery				
Day	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	18	22	23	37	75
2	22	40	42	25	44
3	36	69	9	9	37
4	46	74	52	52	64
5	49	63	53	74	153
Mean	34	54	36	39	75
Standard deviation	14	22	19	25	46

TABLE 83. SURROGATE COMPOUND RECOVERIES IN BOTTOM ASH SAMPLES, PLANT NO. 3

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	50, 43	64, 54	76, 50	83, 67	0, 0
2	33, 43	30, 62	53, 47	66, 82	0, 0
3	36, 19	54, 42	45, 26	55, 47	0, 1
4	39, 41	59, 61	76, 52	88, 61	0, 29
5	33, 32	53, 53	53, 52	81, 62	17, 1
Mean	37	53	53	69	5
Standard deviation	7	6	12	10	7
Average % deviation for duplicates	10	11	14	12	92

TABLE 84. SURROGATE COMPOUND RECOVERIES IN FLY ASH SAMPLES, PLANT NO. 3

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	33, 43	42, 57	41, 56	54, 69	12, 3
2	33, 41	56, 62	80, 62	93, 75	25, 42
3	37, 30	53, 64	61, 82	75, 80	2, 1
4	25, 59	57, 65	42, 101	88, 140	4, 0
5	49, 34	72, 74	66, 58	96, 88	12, 17
Mean	38	60	65	86	12
Standard deviation	3	8	10	19	13
Average % deviation for duplicates	19	7	19	11	30

TABLE 85. SURROGATE COMPOUND RECOVERIES IN ECONOMIZER ASH SAMPLES, PLANT NO. 3

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	22, 22	6, 26	25, 49	30, 55	0, 2
2	20, 35	35, 26	33, 42	69, 80	0, 0
3	30, 51	4, 4	21, 37	35, 33	0, 0
4	27, 25	46, 52	33, 43	57, 52	0, 0
5	26, 31	19, 47	25, 39	30, 84	0, 0
Mean	29	27	34	53	-
Standard deviation	7	17	4	15	-
Average % deviation for duplicates	15	23	21	18	-

TABLE 86. SURROGATE COMPOUND RECOVERIES IN COAL SAMPLES, PLANT NO. 3

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	110, 72	120, 98	120, 99	120, 130	110, 88
2	82, 97	110, 110	150, 86	120, 110	110, 71
3	40, 91	66, 140	26, 120	55, 140	31, 110
4	89, 130	110, 130	140, 140	100, 120	94, 120
5	61, 74	81, 97	69, 260	80, 83	75, 95
Mean	85	106	121	106	90
Standard deviation	18	11	34	17	14
Average % deviation for duplicates	19	13	31	12	21

TABLE 87. SURROGATE COMPOUND RECOVERIES IN PLANT BACKGROUND AIR SAMPLES, PLANT NO. 3

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	44	51	47	71	60
2	41	58	44	130	82
3	37	57	55	81	87
4	32	64	30	59	41
5	44	65	46	98	94
Mean	40	59	44	89	73
Standard deviation	5	6	9	28	22

TABLE 88. SURROGATE COMPOUND RECOVERIES IN LAKE WATER, PLANT NO. 3

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	44	53	67	76	2
2	48	63	66	100	2
3	50	60	74	98	7
4	45	59	72	100	0
5	48	62	67	95	0
Mean	47	59	69	95	2
Standard deviation	2	4	4	11	3

TABLE 89. AVERAGE RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 3

Sample type	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
Flue gas	34 ± 14[a]	54 ± 22	36 ± 19	39 ± 25	75 ± 46
Bottom ash	37 ± 7	53 ± 6	53 ± 12	69 ± 10	5 ± 7
Fly ash	38 ± 3	60 ± 8	65 ± 10	86 ± 19	12 ± 13
Economizer ash	29 ± 7	27 ± 17	34 ± 4	53 ± 15	0
Coal	85 ± 18	106 ± 11	121 ± 34	106 ± 17	90 ± 14
Plant background air	40 ± 5	59 ± 6	44 ± 9	89 ± 28	73 ± 22
Aqueous influent	47 ± 2	59 ± 4	69 ± 4	95 ± 11	2 ± 3

[a] Mean ± standard deviation.

TABLE 90. SURROGATE COMPOUND RECOVERIFS IN FLUE GAS SAMPLES, PLANT NO. 4

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	25	24	22	34	40
2	17	39	20	28	36
3	65	70	47	41	100
4	56	110	51	56	120
5	22	86	47	64	15
Mean	37	65	37	45	63
Standard deviation	22	34	15	15	47

TABLE 91. RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 4

Sample type	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
Flue gas	37 ± 22	65 ± 34	37 ± 15	45 ± 15	63 ± 47
Bottom ash	62, 110	79, 110	51, 76	70, 120	51, 96
Fly ash	50, 87	56, 90	36, 86	52, 101	17, 56
Coal	4, 22	53, 45	0, 23	40, 37	0, 0
Plant background air	ND[a,b]	48[a]	11[c]	15[c]	39[c]
Quench influent	77	37	78	94	0
Quench effluent	76, 58	83, 69	80, 68	91, 72	0, 0

[a] Determined by HRGC/FID.

[b] Co-eluting interferences did not permit determination.

[c] Determined by HRGC/Hall.

TABLE 92. SURROGATE COMPOUND RECOVERIES IN FLUE GAS SAMPLES, PLANT NO. 5

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	58	71	50	42	49
2	53	55	45	50	40
3	49	62	41	54	34
4	65	58	60	68	49
5	46	70	43	63	54
Mean	54	63	48	55	45
Standard deviation	8	7	8	10	8

TABLE 93. SURROGATE COMPOUND RECOVERIES IN PLANT BACKGROUND AIR SAMPLES, PLANT NO. 5

	% Recovery				
Day	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	42	80	44	58	64
2	59	68	64	69	83
3	35	95	43	89	92
4	9	41	13	38	37
5	7	56	10	52	48
Mean	31	68	35	61	65
Standard deviation	22	21	23	19	23

TABLE 94. AVERAGE RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 5

	% Recovery				
Sample type	Naphthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
Flue gas	54 ± 8	63 ± 7	48 ± 8	55 ± 10	45 ± 8
Bottom ash	25, 11	43, 27	30, 17	35, 24	10, 2
Fly ash	26, 65	68, 40	40, 70	64, 83	0, 0
Coal	73	35	72	85	93
Plant background air	31 ± 22	68 ± 21	35 ± 23	61 ± 19	65 ± 23
Quench influent	73	83	84	94	7
Quench effluent	68, 64	51, 32	71, 61	82, 63	42, 26

TABLE 95. SURROGATE COMPOUND RECOVERIES IN FLUE GAS SAMPLES, PLANT NO. 6

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	110	67	78	96	76
2	35	45	21	45	41
3	82	23	71	82	57
4	96	57	73	88	17
5	120	110	84	100	73
Mean	84	60	65	82	53
Standard deviation	33	31	25	22	24

TABLE 96. SURROGATE COMPOUND RECOVERIES IN PLANT BACKGROUND AIR SAMPLES, PLANT NO. 6

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	0	64	50	74	72
2	0	63	52	75	76
3	42	79	49	68	53
4	19	78	39	72	64
5	42	60	41	59	67
Mean	20	69	46	70	67
Standard deviation	21	9	6	6	9

TABLE 97. AVERAGE RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 6

Sample type	% Recovery				
	Naphthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
Flue gas	88 ± 33	60 ± 31	65 ± 25	82 ± 22	53 ± 24
Bottom ash	44, 56	73, 85	42, 58	79, 81	80, 82
Fly ash	0, 4	73, 64	28, 6	72, 63	50, 66
Coal	53, 82	150, 85	67, 76	100, 150	79, 130
Plant background air	20 ± 21	69 ± 9	46 ± 6	70 ± 6	67 ± 9
Quench influent	73, 84	75, 90	69, 65	82, 92	9, 11
Quench effluent	66, 64	89, 65	55, 65	83, 87	2, 0

TABLE 98. SURROGATE COMPOUND RECOVERIES IN FLUE GAS SAMPLES, PLANT NO. 7

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachlorobenzene-$^{13}C_6$	3,4,3',4'-Tetrachlorobiphenyl-d_6	Pentachlorophenol-$^{13}C_6$
1	71	67	43	63	83
2	25	41	25	34	32
3	14	28	13	20	17
4	43	70	41	72	49
5	46	58	47	74	78
Mean	40	53	34	53	52
Standard deviation	22	18	14	24	29

TABLE 99. SURROGATE COMPOUND RECOVERIES IN PLANT BACKGROUND AIR SAMPLES, PLANT NO. 7

Day	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
1	110	71	73	61	53
2	110	83	93	67	83
3	87	48	64	45	59
4	110	76	37	66	27
5	82	77	67	63	76
Mean	100	71	67	61	59
Standard deviation	15	14	20	9	22

TABLE 100. AVERAGE RECOVERIES OF THE SURROGATE COMPOUNDS FOR SAMPLES FROM PLANT NO. 7

Sample type	% Recovery				
	Naphthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
Flue gas	40 ± 22	53 ± 18	34 ± 14	53 ± 24	52 ± 29
Bottom ash	86, 66	77, 88	72, 67	72, 92	79, 96
Fly ash	76, 50	110, 76	84, 64	100, 73	72, 72
Economizer ash	69, 66	83, 79	76, 74	89, 84	38, 50
Coal	64, 50	81, 69	68, 55	74, 61	70, 60
Plant background air	100 ± 15	71 ± 14	67 ± 20	61 ± 9	59 ± 22
Quench influent	69, 62	110, 110	80, 69	87, 92	7, 8
Quench effluent	79, 74	110, 110	82, 83	90, 86	11, 8

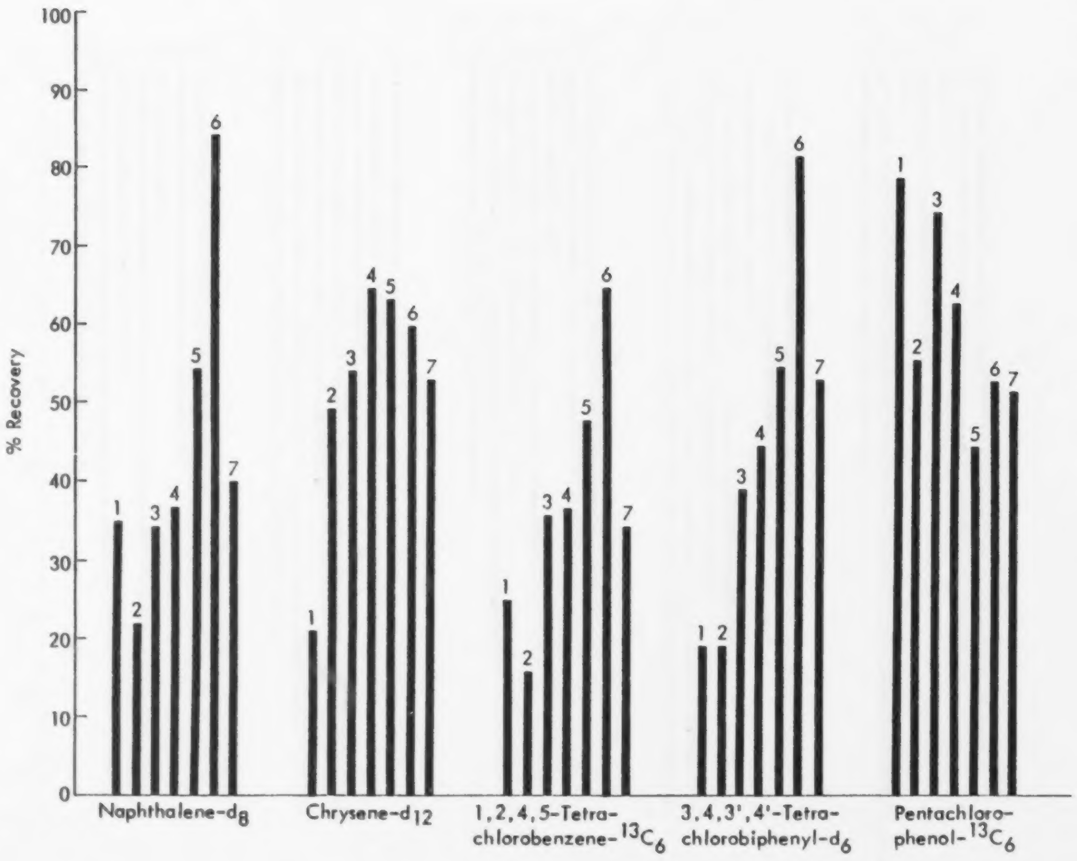

Figure 38. Surrogate compound recoveries from flue gas samples.

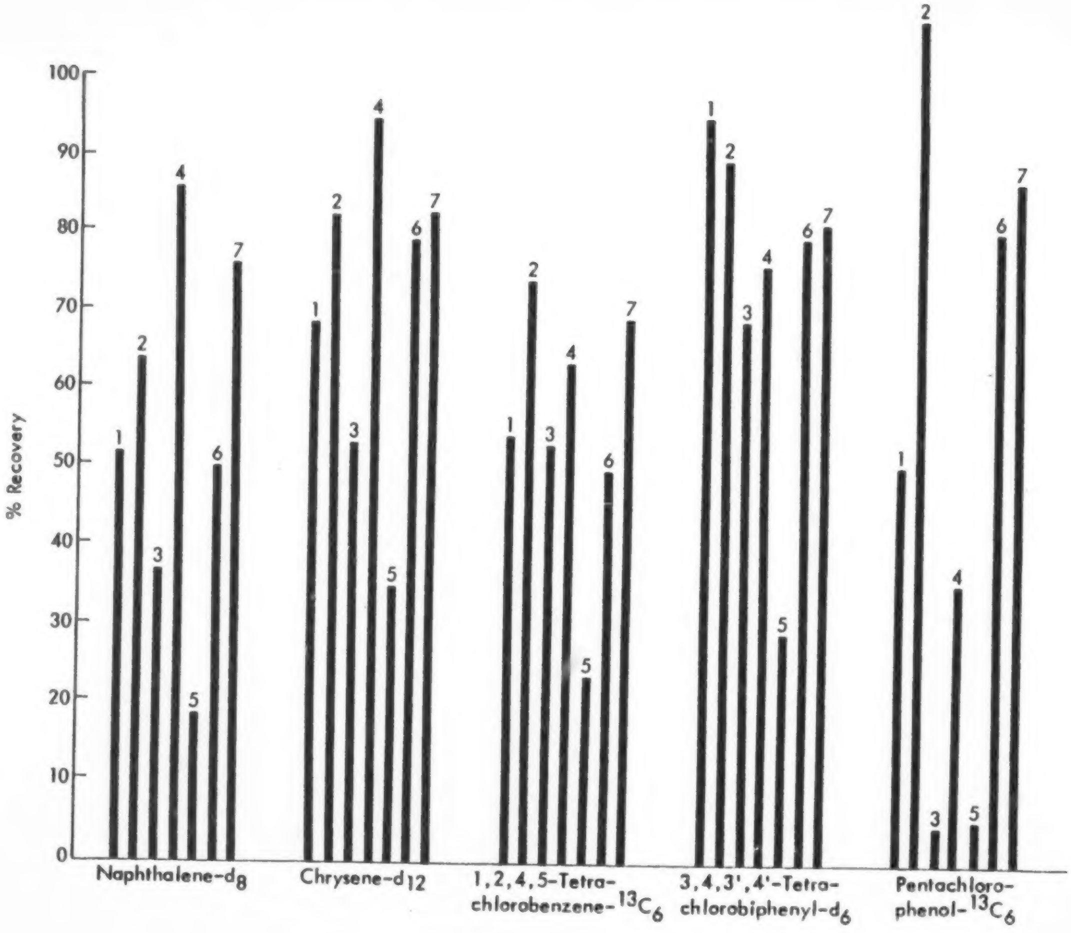

Figure 39. Surrogate compound recoveries from bottom ash samples.

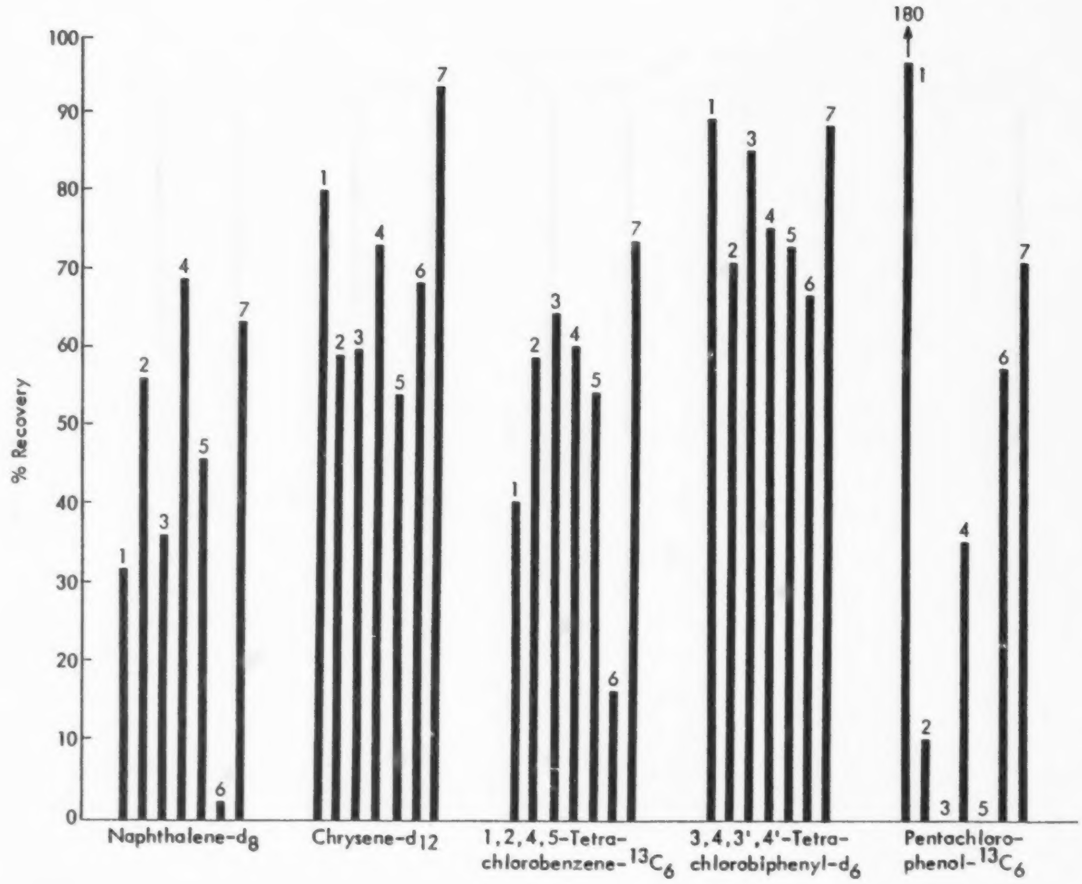

Figure 40. Surrogate compound recoveries from fly ash samples.

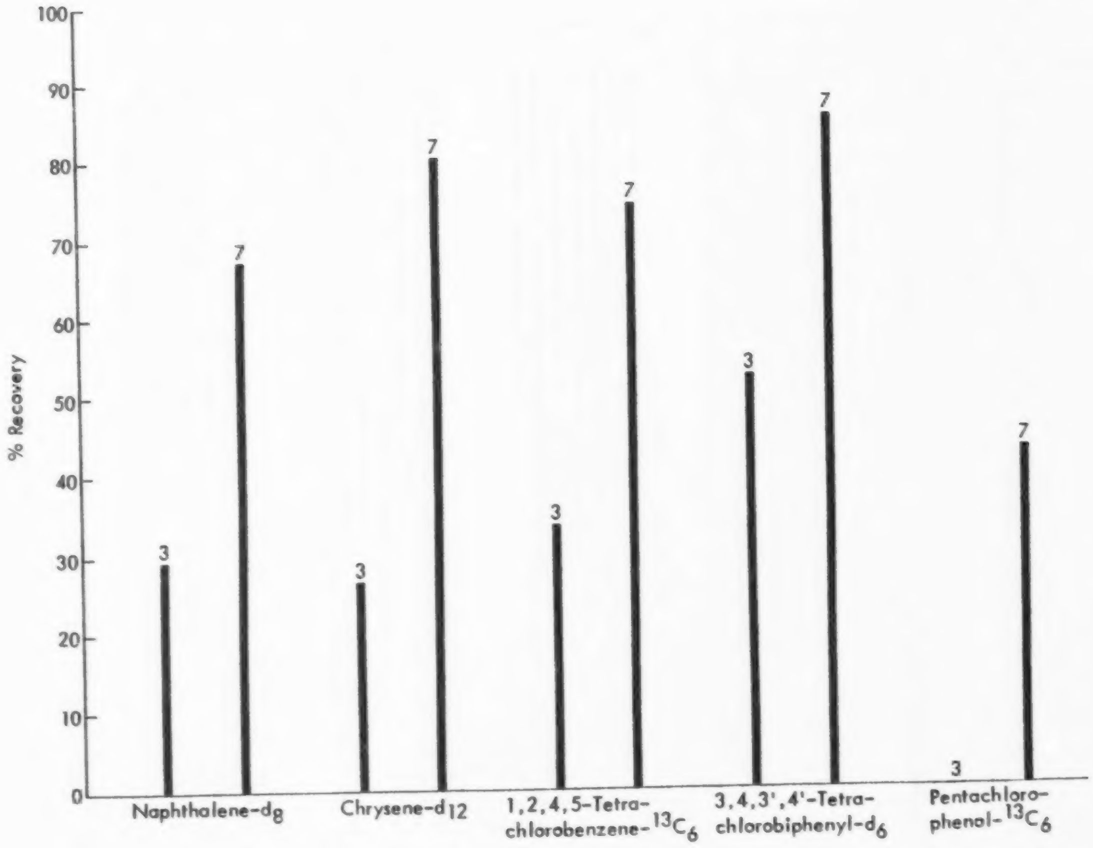

Figure 41. Surrogate compound recoveries from Economizer ash samples.

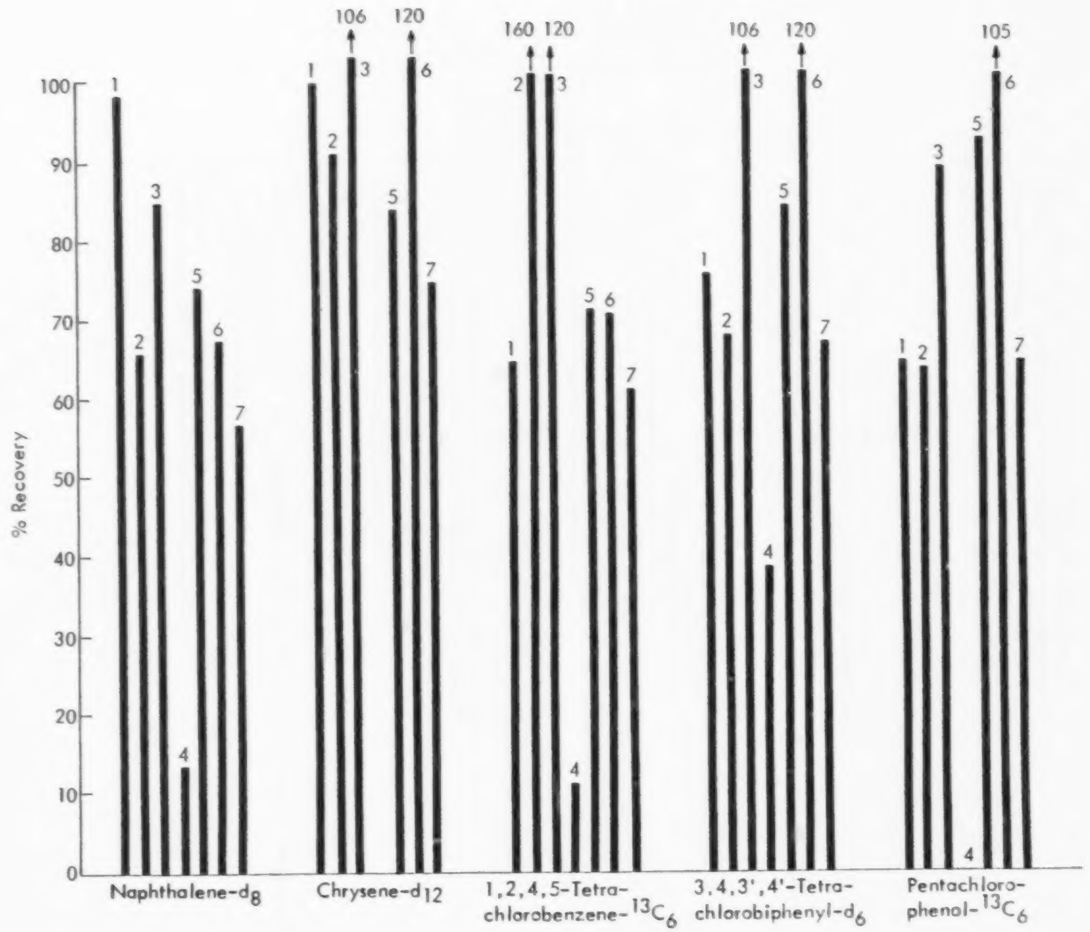

Figure 42. Surrogate compound recoveries from coal samples.

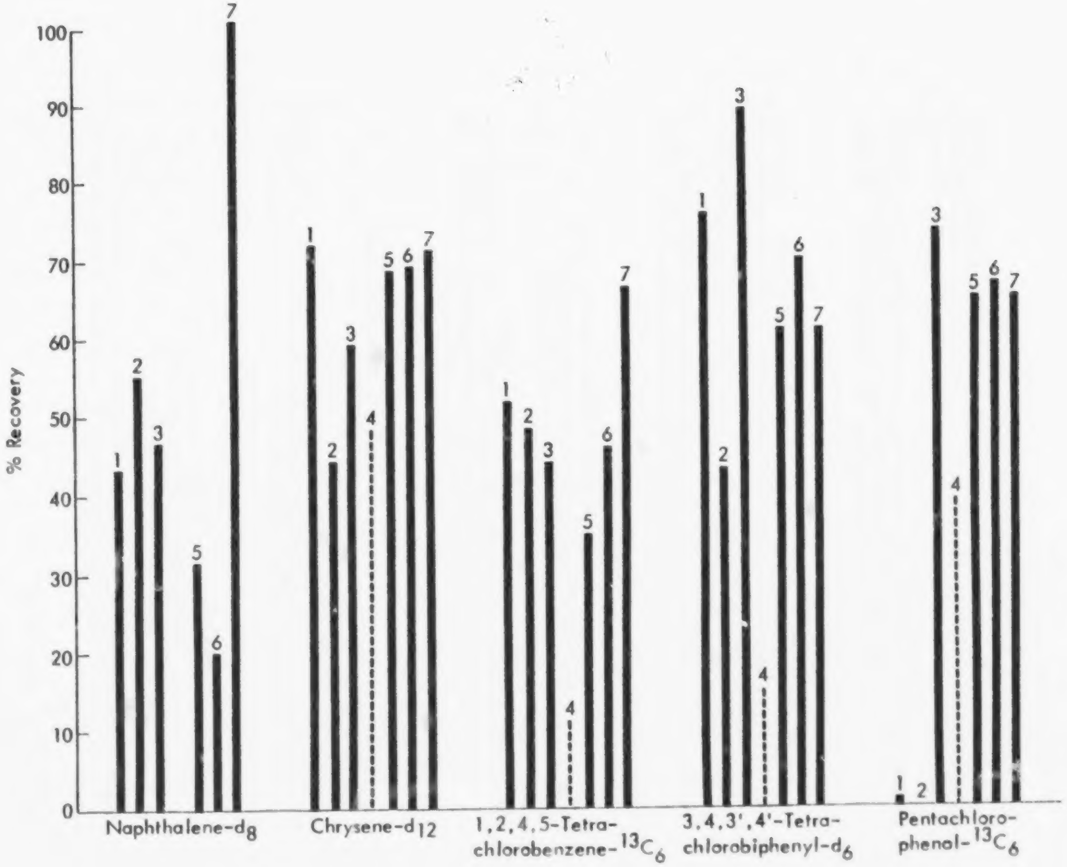

Figure 43. Surrogate compound recoveries from plant background air samples. Data for Plant No. 4 from HRGC/Hall-FID.

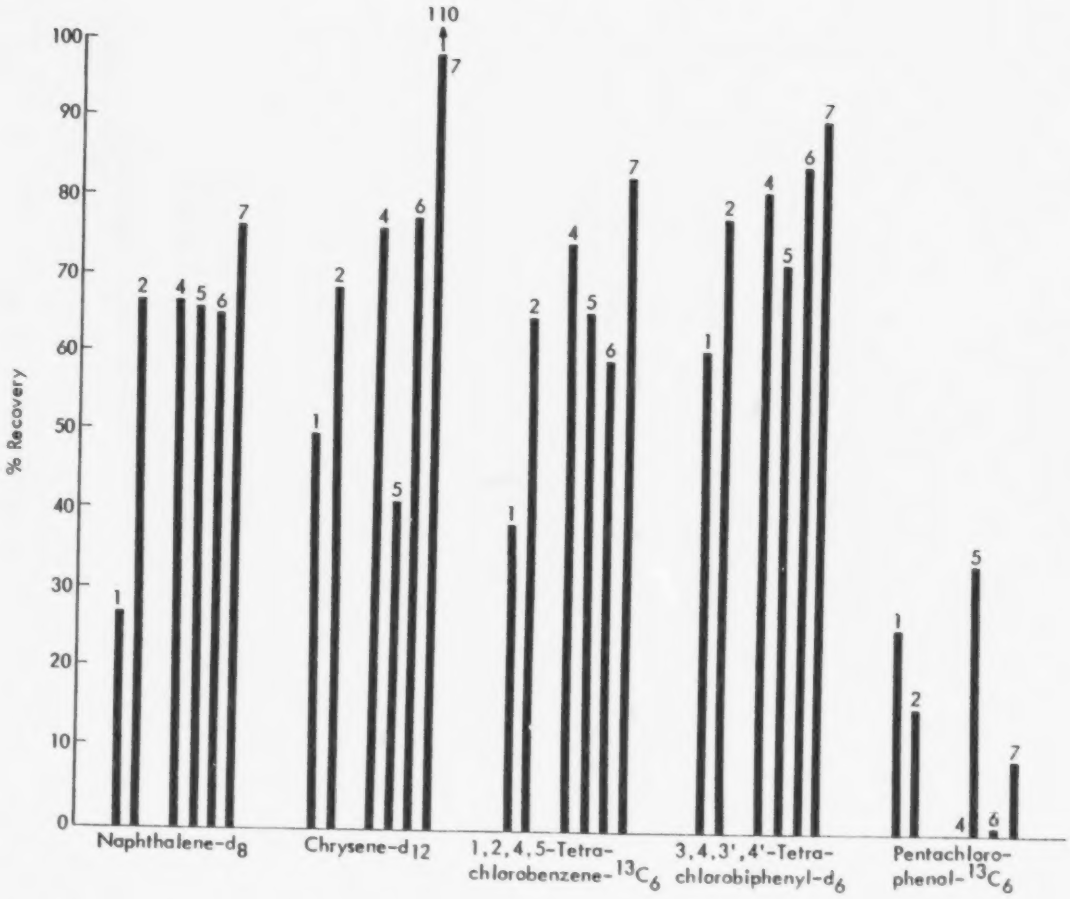

Figure 44. Surrogate compound recoveries from quench effluent water samples.

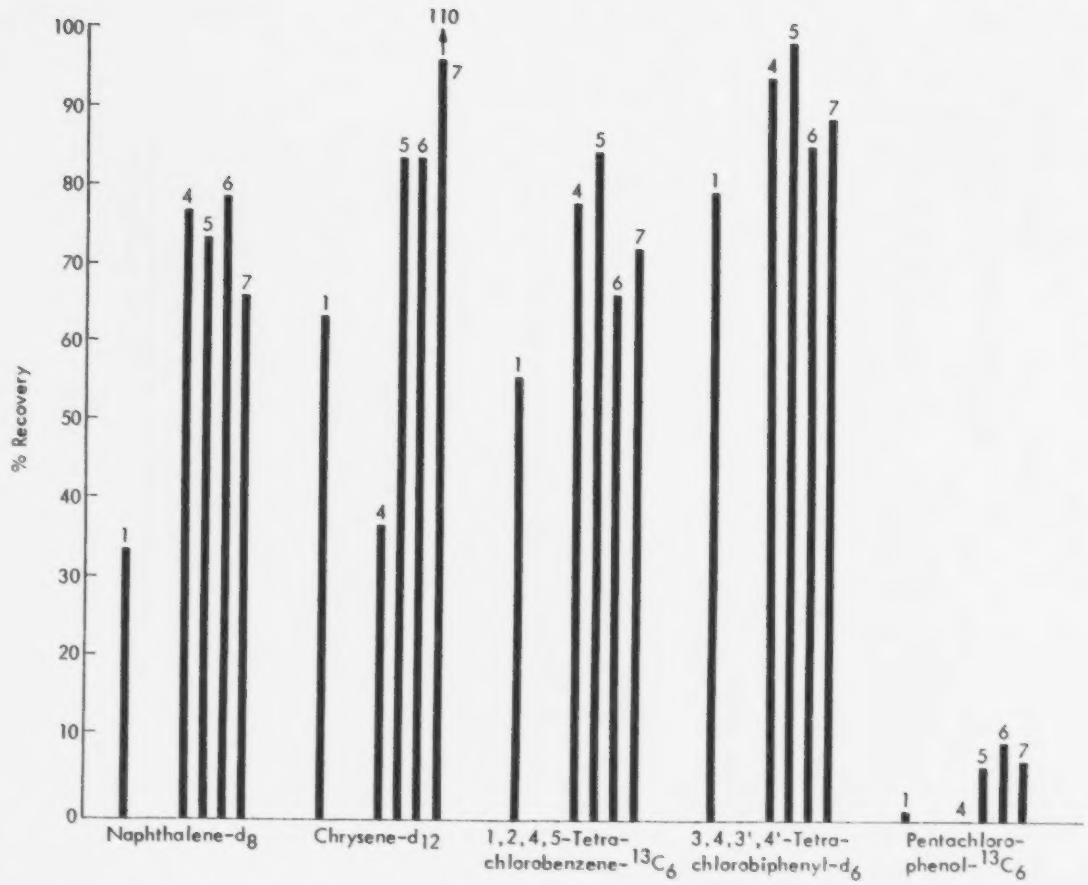

Figure 45. Surrogate compound recoveries from quench influent water samples.

TABLE 101. AVERAGE SURROGATE COMPOUND RECOVERY (%) FOR ALL SAMPLE MEDIA FROM ALL SEVEN PLANTS

Sample media	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
Flue gas	44 ± 21	52 ± 15	37 ± 16	45 ± 22	60 ± 13
Bottom ash	55 ± 23	71 ± 20	55 ± 17	74 ± 22	60 ± 40
Fly ash	44 ± 23	70 ± 14	53 ± 19	79 ± 9	53 ± 63
Economizer ash[a]	29, 68	27, 81	34, 75	53, 87	0, 44
Coal	65 ± 27	82 ± 31	80 ± 46	82 ± 27	69 ± 35
Plant background air[b]	48 ± 28	64 ± 11	49 ± 11	67 ± 16	44 ± 34
Aqueous influent	65 ± 19	75 ± 27	72 ± 11	89 ± 6	5 ± 4
Aqueous effluent	61 ± 17	70 ± 24	64 ± 15	78 ± 10	14 ± 14

[a] For Plant Nos. 3 and 7 only.

[b] Results for Plant No. 4, determined by HRGC/Hall-FID, were not averaged.

TABLE 102. SUMMARY OF SURROGATE COMPOUND RECOVERY FOR FLUE GAS SAMPLES WITH RESPECT TO THE SAMPLING TRAIN COMPONENT SPIKED

Component[a]	% Recovery				
	Napthalene-d_8	Chrysene-d_{12}	1,2,4,5-Tetrachloro-benzene-$^{13}C_6$	3,4,3',4'-Tetrachloro-biphenyl-d_6	Pentachloro-phenol-$^{13}C_6$
XAD-resin	50 ± 29	54 ± 27	39 ± 24	47 ± 28	67 ± 27
Probe rinse	43 ± 27	55 ± 23	41 ± 22	49 ± 25	61 ± 36
Filter	38 ± 29	45 ± 23	27 ± 26	35 ± 26	55 ± 32

[a] A single component of each train was spiked with surrogate compounds according to the selection schedule described in Section 6. Hence, each recovery shown here represents the recovery for the entire train.

CAPILLARY COLUMN PERFORMANCE

The five component surrogate standard was analyzed daily by HRGC/Hall-FID and scanning HRGC/MS. Peak shape and response data were recorded. When the column performance was not satisfactory, remedial action was taken to improve performance. Typically, this required breaking off several inches of the injection end of the column. If the remedial action did not result in satisfactory performance, a new column was installed. A column performance mixture was used to evaluate the columns used for HRGC/Hall screening at least once per week during use. The mixture contained several halogenated, nonpolar and polar compounds which were used to calculate acid-base character of the column (pH), the number of theoretical plates, (N), the height equivalent to a theoretical plate (HETP), and the adsorption and asymmetry of the test mixture compounds. Figures 46 to 50 show charts of the performance of the fused silica columns used for HRGC/Hall-FID screening during this study. The pH was calculated as the ratio of responses for equal quantities of 4-bromo-2,6-dimethylaniline versus 4-bromo-2,6-dimethylphenol. A neutral column should give a value equal to 1.0. The plot of pH versus date (Figure 46) indicates that the columns used were usually slightly acidic in character. The number of theoretical plates, N (Figure 47) and the HETP value (Figure 48) reported were calculated for 1-bromoundecane. The adsorption ratios (Figure 49) were determined by comparing the peak height for test compounds susceptible to adsorption with that of an inert compound, 1-bromo-undecane. The asymmetry was calculated for each peak of the test mixture from the formula.

$$As = \frac{W_b}{W_f} \times 100$$

where W_b and W_f are the back and front baseline widths of the peak measured from a line bisecting the peak maximum. A perfectly symmetrical peak should have an asymmetry value of 100. However, the Hall detector response created tailing of the peaks in the test mixture and the optimum asymmetry for this detector response is actually greater than 100 as indicated in Figure 50.

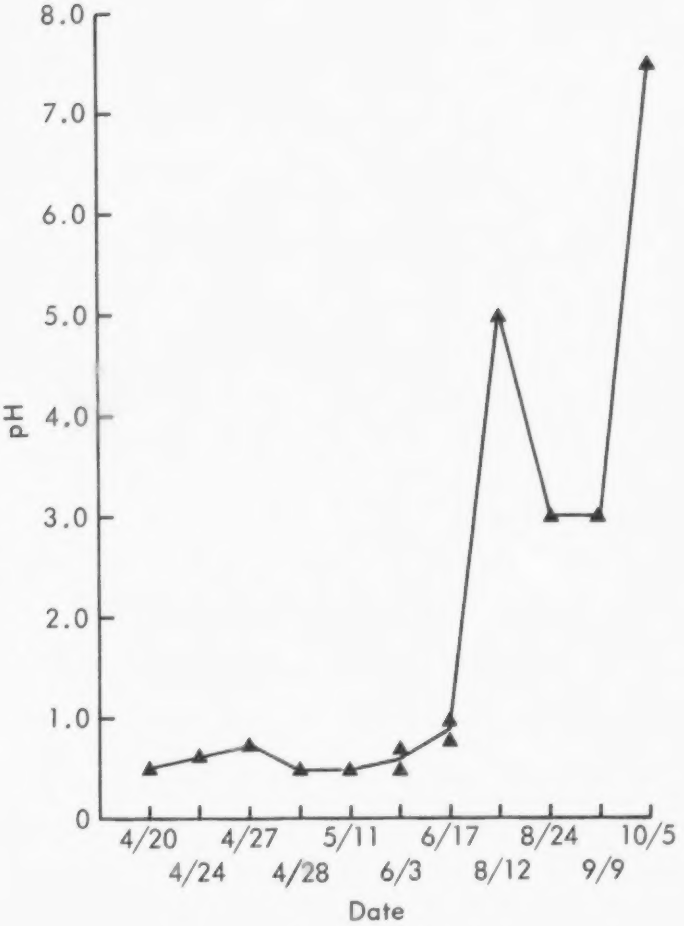

Figure 46. Fused silica column pH versus time as calculated from the response of equal quantities of 4-bromo-2,6-dimethylphenol and 4-bromo-2,6-dimethylaniline

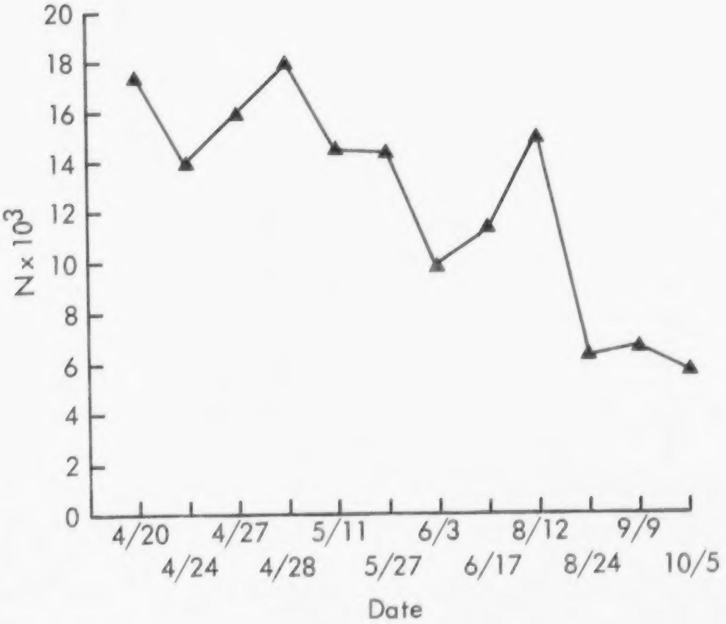

Figure 47. Number of theoretical plates (N) versus time for a fused silica capillary column.

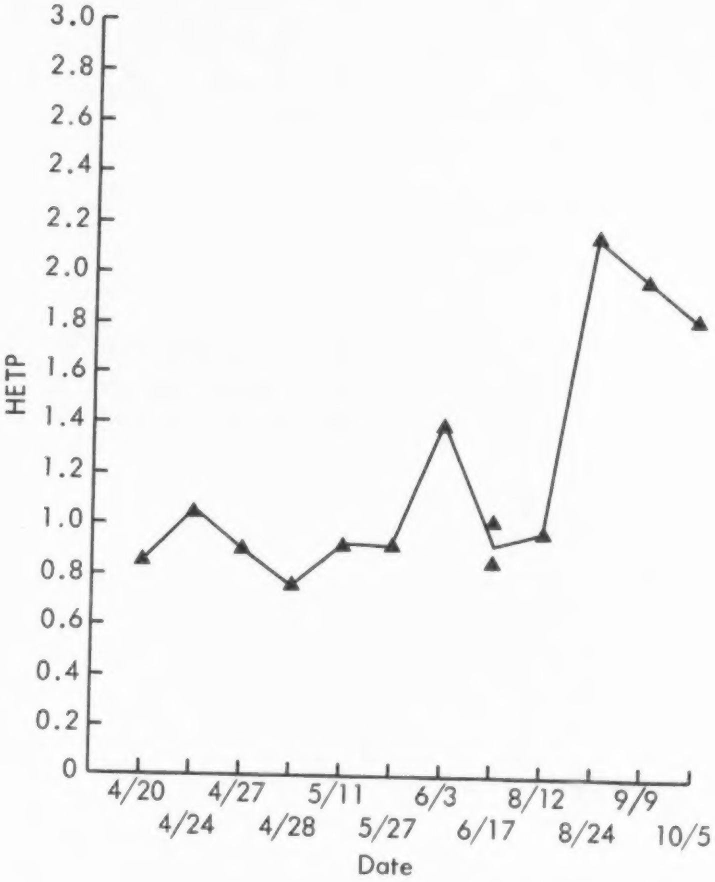

Figure 48. Calculated HETP versus time for a fused silica capillary column.

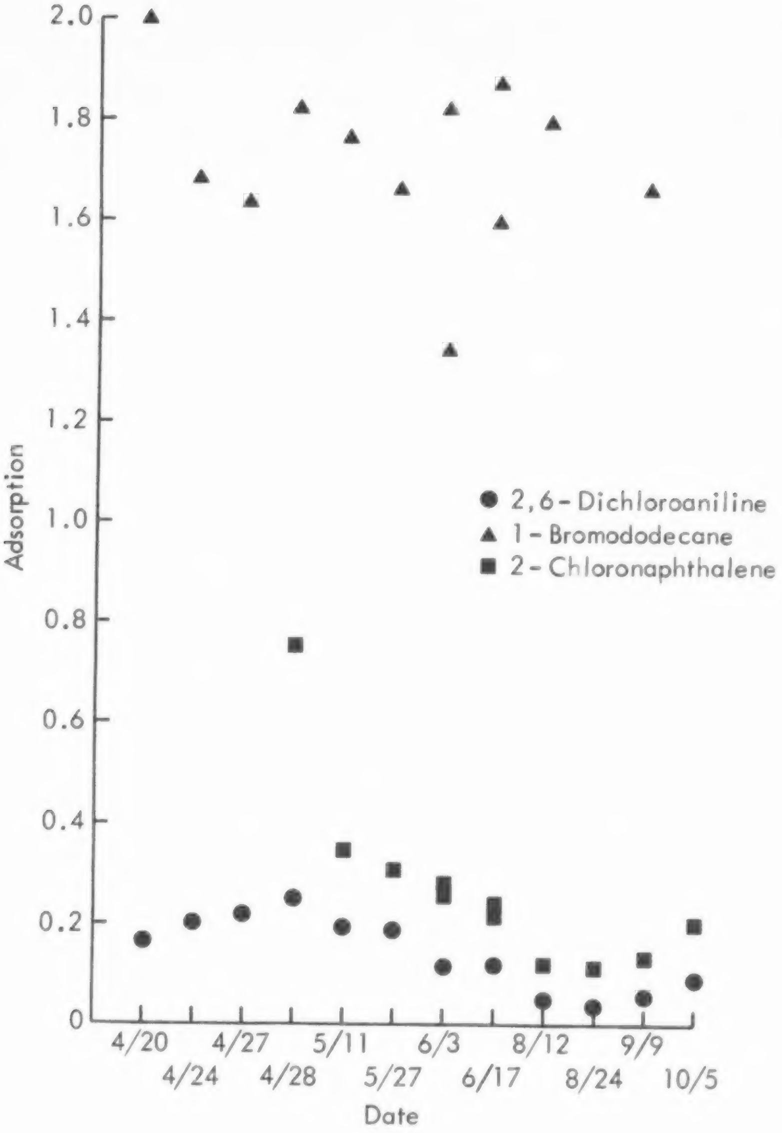

Figure 49. Adsorption versus time for selected compounds on a fused silica capillary column.

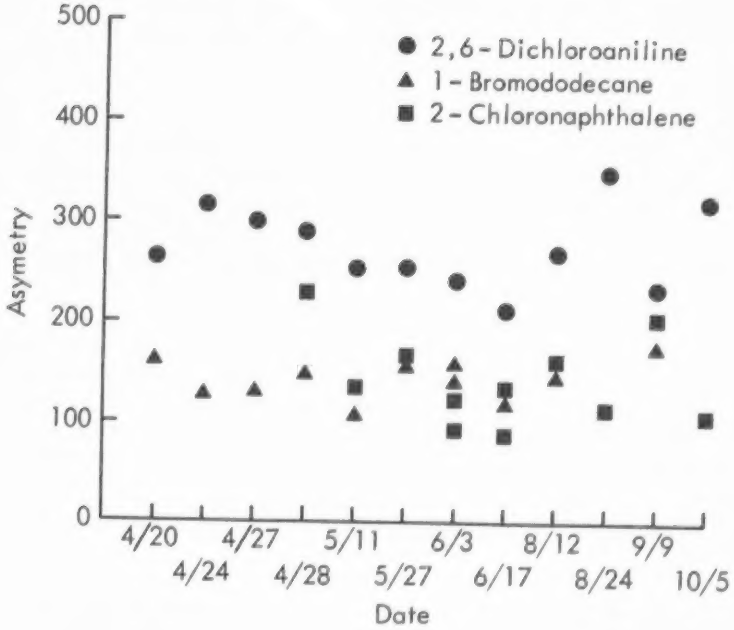

Figure 50. Asymmetry versus time for selected compounds on a fused silica capillary column.

SECTION 10

EMISSIONS RESULTS

The emission rates for the target PAH and phthalate compounds determined in flue gases for the seven coal-fired power plants are shown in Table 103. The emission rates were calculated from the concentrations of each compound in the flue gases (presented in Section 8) and the flue gas volume flow rates (presented in Section 7). Average emission rates for each compound identified in flue gases for the 5-day sampling period at each plant are shown in Table 104. The emission rates for most compounds were generally similar for all plants except Plant No. 3. In general, emission rates were lower for Plant No. 3.

The emission rates for total PCBs in flue gases at the seven plants are shown in Table 105. The average emission rates for each plant are shown in Table 106 with the average PCB input rates determined for plant background air. Although the average emission rates for each plant were all higher than the input rates attributed to plant background air, the input rates were all within one standard deviation of the 5-day average emission rates for five of the seven plants.

The exact origin of the PCBs in the flue gas emissions from the coal-fired power plants cannot be determined from the data presented from this investigation. However, some of the possible sources for PCBs suggested by Richards and Junk[5] include (a) degassing of fuel; (b) air used to support the combustion; (c) contamination from components of the ducts leading to and from the combustion zone; (d) chlorination of biphenyl in or after the combustion zone; and (e) the formation in the combustion zone by a series of complex reactions.

PCDDs and PCDFs were not identified in the flue gas samples. The method detection limits were comparable to those achieved for the pilot study for municipal incinerator flue gas samples that contained several PCDD and PCDF isomers. An estimated worst case emission rate for TCDD or TCDF from the coal-fired power plants based solely on the method detection limit (assuming 100%) recovery would be in the range of 100 to 500 µg/hr.

TABLE 103. CONCENTRATIONS AND EMISSION RATES FOR TARGET COMPOUNDS IN FLUE GASES (μg/dscm) AND EMISSION RATES (mg/hr) FROM THE SEVEN COAL-FIRED POWER PLANTS

Compound	Composite day	Plant No. 1 Flue gas conc. (μg/dscm)	Plant No. 1 Emis. rate (mg/hr)	Plant No. 2 Flue gas conc. (μg/dscm)	Plant No. 2 Emis. rate (mg/hr)	Plant No. 3 Flue gas conc. (μg/dscm)	Plant No. 3 Emis. rate (mg/hr)	Plant No. 4 Flue gas conc. (μg/dscm)	Plant No. 4 Emis. rate (mg/hr)	Plant No. 5 Flue gas conc. (μg/dscm)	Plant No. 5 Emis. rate (mg/hr)	Plant No. 6 Flue gas conc. (μg/dscm)	Plant No. 6 Emis. rate (mg/hr)	Plant No. 7 Flue gas conc. (μg/dscm)	Plant No. 7 Emis. rate (mg/hr)
Naphthalene	1	0.37	2,040	0.57	490			0.43	750	1.2	5,500	1.0	1,400	0.48	710
	2	0.28	1,500			0.10	99	0.51	890	1.1	4,700	0.45	640	0.14	190
	3	0.32	1,800	1.7	1,500	0.53	520	1.5	2,500	0.86	3,800	1.3	1,900	0.57	720
	4	0.17	980	3.8	3,400	1.4	1,400	2.0	3,500	2.2	8,200	6.0	8,100	0.44	520
	5	0.34	970	2.5	2,200	0.33	320	0.78	1,100	0.83	2,600	1.1	1,600	0.65	780
Acenaphthylene	1														
	2														
	3			0.32	290										
	4														
	5	0.66	190												
Acenaphthene	1														
	2			tr[a]											
	3														
	4			tr											
	5														
Fluorene	1	0.018	100												
	2	0.015	79					tr							
	3			0.67	600			0.033	57						
	4							0.070	120					0.012	16
	5														
Phenanthrene	1	0.21	1,170	0.42	360	0.06	57	0.071	130			0.95	130	0.045	66
	2	0.22	1,210					0.083	140			0.056	140	0.0064	9
	3			7.8	6,950			0.14	240			0.12	170	0.078	100
	4	0.14	720	1.4	1,200	0.10	98	0.24	410			0.13	180	0.037	44
	5	0.33	950	0.26	240	0.07	71	0.21	310			0.26	380	0.072	87
Fluoranthene	1	0.088	490												
	2	0.044	240												
	3			1.15	1,030										
	4	0.044	220					0.088	150						
	5							0.058	85						
Pyrene	1	0.057	310												
	2	0.024	130												
	3			0.32	290										
	4														
	5														
Chrysene	1	0.031	170												
	2					tr						0.070	100		
	3			0.75	670			0.048	82						
	4			0.14	120	tr		0.12	210	0.007	26				
	5											0.045	65		

(continued)

TABLE 103 (continued)

Compound	Composite day	Plant No. 1		Plant No. 2		Plant No. 3		Plant No. 4		Plant No. 5		Plant No. 6		Plant No. 7	
		Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)	Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)	Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)	Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)	Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)	Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)	Flue gas conc. (µg/dscm)	Emis. rate (mg/hr)
Benzo[a]-pyrene	1														
	2	0.006	34												
	3														
	4														
	5														
Dimethyl-phthalate	1	0.15	860												
	2	0.13	710									0.54	780	0.060	83
	3														
	4	0.071	360	tr											
	5														
Diethyl-phthalate	1	6.0	33,400	8.7	7,470	0.42	410								
	2	4.1	21,900			2.3	2,200	0.79	1,400						
	3	1.9	10,700	6.5	5,760			5.0	8,400						
	4	5.8	29,400	6.8	6,160			12.3	21,100						
	5	10.5	30,100	4.1	3,670	0.49	480	11.7	17,300						
Di-n-butyl-phthalate	1	9.1	50,600	28.3	24,300										
	2	4.0	21,600			0.10	94	1.7	3,000						
	3	0.98	5,400	41.6	37,100										
	4	3.1	15,700	2.2	2,010										
	5	6.7	19,200	1.8	1,600										
Butylbenzyl-phthalate	1	1.1	6,000			0.35	340								
	2	0.64	3,500			0.29	280	0.45	780						
	3			4.0	3,500	tr		0.50	860						
	4	0.44	2,200					0.64	1,100						
	5	1.8	5,200	1.3	1,100	0.46	440	tr							
Bis(2-ethyl-hexyl)-phthalate	1	12.3	68,500	5.0	4,280	2.7	2,600			21	93,000	34	48,000	0.53	790
	2	9.1	48,900			5.2	5,100			3.4	15,000	0.93	1,300	0.82	1,100
	3					25	24,200	15.3	26,100	9.2	40,000	11	16,000	1.4	1,700
	4	13.5	68,000			24	23,300	3.4	5,800	30	110,000	8.3	11,000	6.7	7,800
	5	7.4	21,200			6.8	6,600	31.2	46,000	8.6	27,000	0.55	800	18	22,000
Di-n-octyl-phthalate	1	1.1	5,900			0.93	910	0.63	1,100	2.0	8,800				
	2	4.9	26,200					0.31	540						
	3	0.23	1,300					0.54	910	0.50	2,200				
	4	2.5	12,600					1.2	2,000						
	5	1.7	4,800												

---

a tr = ≲ 0.025 µg/dscm.

TABLE 104. AVERAGE EMISSION RATES OF TARGET PAH COMPOUNDS IN FLUE GASES

Compound	Emission rates (mg/hr)						
	Plant No. 1	Plant No. 2	Plant No. 3	Plant No. 4	Plant No. 5	Plant No. 6	Plant No. 7
Naphthalene	1,400	1,500	470	1,700	5,000	2,700	580
Acenaphthylene	38	72					
Fluorene	36	120		35			3
Phenanthrene	810	1,800	45	250		200	61
Fluoranthene	190	210		47			
Pyrene	88	58					
Chrysene	34	160		110	5	33	
Benzo[*a*]pyrene	7						
Dimethylphthalate	390					160	170
Diethylphthalate	25,000	4,600	620	9,600			
Di-*n*-butylphthalate	23,000	13,000	19	600			
Butylbenzylphthalate	3,400	920	210	550			
Bis(2-ethylhexyl)phthalate	41,000	860	11,000	16,000	57,000	15,000	6,700
Di-*n*-octylphthalate	10,000				2,200		

TABLE 105. FLUE GAS OUTLET CONCENTRATIONS OF TOTAL POLYCHLORINATED BIPHENYLS (PCBs) AND EMISSION RATES FOR PLANTS 1 THROUGH 7

	Concentration (µg/dscm)	Emission rate (mg/hr)
Plant 1		
Day 1	3.1	17,200
Day 2	2.0	10,700
Day 3	0.2	1,100
Day 4	2.4	12,200
Day 5	0.5	1,400
	Mean =	8,500
	S.D. =	7,100
Plant 2		
Day 1	0.18	150
Day 2	0.63	550
Day 3	0.32	290
Day 4	1.04	940
Day 5	0.10	90
	Mean =	400
	S.D. =	350
Plant 3		
Day 1	0.0482	47
Day 2	0.0026	2.5
Day 3	0.0012	1.2
Day 4	≦ 0.0005	≦ 0.5
Day 5	≦ 0.0005	≦ 0.5
	Mean =	10
	S.D. =	21
Plant 4		
Day 1	4.6	8,100
Day 2	0.8	1,400
Day 3	1.4	2,400
Day 4	1.8	3,100
Day 5	0.5	700
	Mean =	3,100
	S.D. =	2,900

(continued)

TABLE 105 (continued)

	Concentration (μg/dscm)	Emission rate (mg/hr)
Plant 5		
Day 1	0.020	89
Day 2	0.008	35
Day 3	0.014	62
Day 4	0.012	44
Day 5	≦ 0.004	≦ 12
		Mean = 48
		S.D. = 29
Plant 6		
Day 1	0.43	610
Day 2	0.17	250
Day 3	0.014	20
Day 4	0.074	81
Day 5	0.44	640
		Mean = 320
		S.D. = 290
Plant 7		
Day 1	0.014	20
Day 2	≦ 0.002	≦ 3
Day 3	≦ 0.002	≦ 3
Day 4	0.014	17
Day 5	0.094	114
		Mean = 31
		S.D. = 47

TABLE 106. AVERAGE PCB INPUTS AND EMISSIONS (PLANT BACKGROUND AIR AND FLUE GAS OUTLET)

Plant No.	Inputs - plant background[a] air (mg/hr)	Emissions - flue gas (mg/hr)
1	1,130	8,500 ± 7,100
2	220	400 ± 356
3	ND[b]	≦ 0.5
4	1,740	3,100 ± 2,900
5	28	48 ± 29
6	4.5	320 ± 290
7	5	31 ± 47

[a] PCB levels in combustion air samples were determined as 5-day composites.

[b] ND = not detected.

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APPENDIX

SAMPLING AND ANALYSIS METHODS MANUAL

SAMPLING AND ANALYSIS PROCEDURES FOR ASSESSING ORGANIC EMISSIONS FROM STATIONARY COMBUSTION SOURCES IN EXPOSURE EVALUATION DIVISION COMBUSTION STUDIES

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METHODS MANUAL

EPA Contract No. 68-01-5915
MRI Project No. 4901-A(36)

Prepared for:

U.S. Environmental Protection Agency
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DISCLAIMER

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PREFACE

This sampling and analysis document was prepared for the Environmental Protection Agency under EPA Contract No. 68-01-5915. The methods described in this document were designed for use by Midwest Research Institute in assessments of stationary combustion source emissions. They may also be used as guidelines by other researchers who wish to conduct comparable studies. This document was prepared by Dr. John S. Stanley, Dr. Clarence L. Haile (MRI Task Manager), Ms. Ann M. Small, and Mr. Edward P. Olson.

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December 1, 1981

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SECTION 1

INTRODUCTION

The sampling and analysis methods described in this report were specifically designed for use in an ongoing nationwide survey of emissions of organic pollutants from stationary combustion sources. The primary focus of this survey is on polynuclear aromatic hydrocarbons (PAHs) and polychlorinated aromatic hydrocarbons including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). To date, these procedures have been used by Midwest Research Institute (MRI) to survey emissions from coal-fired utility boilers, a co-fired (coal + refuse-derived fuel) utility boiler, and a municipal refuse incinerator. This document was prepared by MRI solely as a guideline for other laboratories who may participate in the same study, and for other researchers who wish to use these methods.

SECTION 2

SAMPLING

The procedures described in this section have been used by MRI in obtaining representative samples of the inputs and the emissions from stationary conventional combustion sources. These procedures encompass the specific requirements for site surveys, pretest preparations, and actual sampling procedures. A quality assurance program and sample control and custody documentation procedures are also presented.

The precise sampling procedures used for a specific plant may vary somewhat depending on the specific configuration and operation of the facility. The samples that should be collected include gaseous, solid, and liquid materials. Gaseous emissions should be collected by the EPA Method 5 procedures[1] modified for the capture of trace organic compounds as described in this section. The solid and liquid samples should be collected according to a sound, statistically designed 24-hr schedule.

These methods were designed to provide both qualitative and quantitative information on polycyclic and chlorinated organic compounds. Therefore, it is imperative that the sampling procedures should be followed as closely as possible to prevent contamination or compromise the integrity of the samples.

MEDIA SELECTION

The sample collection program should be designed to allow accurate assessments of the organic pollutants in both input to and emissions from the combustion process. Although the focus of this project is on organic compounds that likely undergo considerable chemical changes in the combustion process, the media selection criteria are the same as would be used to determine a mass balance for a conservative pollutant, e.g., a nonvolatile metal. It is of paramount importance that the collection procedures provide the most representative specimens of the media selected.

The specific media and sampling points for each plant will depend somewhat on the specific design of the plant. However, the media can be described in three categories: inputs, emissions, and miscellaneous media. The principal inputs to the combustion process are fuels and combustion air. All primary fuels should be sampled. Fuels used only for unit startup should be excluded from the sampling program. Combustion air can be sampled near the air intake for the unit. However, care should be taken to avoid collection of fugitive dust that may be suspended by the activities of the sampling equipment or personnel.

The principal emission media are the bottom ash, i.e., the residue from the combustion process, and the flue gases with associated fly ash. Flue gas emissions may have the most widespread impact on the quality of the surrounding environment. Hence, flue gas samples must be collected at a point downstream of the unit's particulate emissions control systems. However, the materials collected by air pollution control devices must also be sampled to allow accurate characterization of the total plant emissions. For example, many coal-fired utility boilers employ electrostatic precipitators (ESPs) to control particulate emissions. The fly ash collected in the ESP hoppers of these plants must be included in the sampling program. In addition, ash that is removed from flue gases by economizers in many plants must also be sampled where practical.

Miscellaneous sample media include other materals that may have direct contact with the combustion products. Examples are the input and overflow waters from a bottom ash wet quenching system. These secondary emission media may pose environmental hazards depending on the plant disposal practices.

A list of typical sample capture requirements for several materials is given in Table 1. Included are sample size, storage container type and size, sampling frequency, and total samples obtained each day. No compositing should be done in the field. All samples should be placed in the appropriate containers prepared as outlined in the pretest preparation and setup procedures.

PRESAMPLING SITE VISIT

Representatives from EPA and the sampling crew chief must consult with the plant supervisor to determine where and how each type of sample may be captured. The crew chief should obtain data on key parameters related to flue gas sampling. These parameters include the stack dimensions, flue gas temperatures, moisture content, static pressure, and flue gas velocities.

Sampling points for grab samples should be located as close as possible to the actual combustion process to avoid sampling combined streams (e.g., from multiple units) or combined waste media (e.g., ash-water mixtures) and to prevent dilution of the desired sample. These precautions should allow simpler data assessments. It is also advantageous to centralize the sampling locations if possible such that the sampling schedules can be followed accurately by the sampling crew. Where possible, special aids for obtaining the samples in a safe and efficient manner should also be considered. Plant staff-operated equipment, limited access areas, special tools, electrical outlets, and periodic safety calls are some possible considerations.

Once all possible sampling points are determined, a statistically sound, random sampling scheme should be provided for solid/liquid sampling that corresponds with the flue gas sampling activities. The sampling schedule should be constructed to provide the sampling team with the specific time and location a sample will be taken. It may be necessary to follow an assigned grid pattern or port selection scheme in order to effectively subsample large surface areas. In addition, sampling schedules may be subject to change each day.

TABLE 1. SAMPLE CAPTURE REQUIREMENTS

Material	Storage size/type	Sample frequency	Total samples (24 hr)
Solid			
Coal	1 qt amber glass	Twice per shift	6
Refuse or RDF[a]	1 qt amber glass	Twice per shift	6
Bottom ash	1 pt amber glass	Twice per shift	6
Fly ash	1 pt amber glass	Twice per shift	6
Other solid waste	1 pt amber glass	Twice per shift	6
Gaseous			
Dry particulate	1 pt amber glass	One per train[c]	2
Reeve Angel 934 AH filter[b]	150 mm X 15mm glass petri dish	One per train[c]	2
Nozzel, probe, cyclone and flask combined rinses	1 qt amber glass (may require additional 250 ml of same)	One per train	2
Sorbent trap	Traps capped with plugs.	One per train	2
First impinger with rinses	950 ml amber glass (may require additional 250 ml of same)	One per train	2
Control 934 AH filter[b]	150 mm X 15 mm glass petri dish	One per day	1
Combustion air	Sorbent trap capped with plugs	One per day	1
Liquid			
Effluent water	1 qt amber glass	Twice per shift (duplicates)	12
Influent water	1 qt amber glass	One per day (duplicate)	1

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[a] Refuse - derived fuel.

[b] Or equilvalent.

[c] Dry particulate will be collected only from trains using a cyclone trap. This trap may not be necessary if particulate loading is light.

[d] Additional filters may be necessary if particulate loading is high.

The presampling site visit should also allow the crew chief to determine local sources for expendable sampling supplies. In addition, the most convenient accommodations for the sampling crew during the testing period should be located.

FLUE GAS SAMPLING EQUIPMENT AND MATERIALS

The modified Method 5 train, shown schematically in Figure 1, is used to collect samples for organic compounds from the stack. (See Note below.) Additional empty impingers may be added just after the first impinger to retain water from high moisture gases. This train should be operated according to Method 5 specific procedures modified by the additional cleanup and recovery procedures required for organic compounds.

The sampling probe liners must be glass or TFE, depending on the flue gas temperature. A glass cyclone should be provided for high particulate gases to avoid excessive filter loading. Vaporous organics are collected by a sorbent trap (Figure 2). This trap is located in the sample line downstream of the heated oven and upstream of the first impinger. The trap is packed with precleaned XAD-2. The module that houses the sorbent trap is water-jacketed. Cold water from an ice bath surrounding the impingers is pumped through the jacket to maintain an outlet temperature of $\leqq$ 16°C (60°F). Because of the possible sensitivity of potential analytes to ultraviolet light all sorbent traps should be kept wrapped in aluminum foil.

All solvents used for preparing the sampling train for testing and for field laboratory cleaning of sample trains should be stored in glass or TFE bottles. All solvents should be Burdick and Jackson Distilled-in-Glass or equivalent grade. TFE or stainless steel forceps should be used for handling filters. The train and train components that contact the sample should be handled with clean, bare hands, i.e., without gloves.

Flue Gas Sampling Pretest Preparation

All train components that will contact the sample (probe, cyclone, filter holder, resin cartridge, and connecting tubes) must be clean of all potentially interfering materials. Component joints that have been previously treated with a sealant, such as silicone grease, must be thoroughly cleaned before use. The recommended procedure for removing Dow Corning High Vacuum

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NOTE: The collection efficiencies for PCBs, PCDDs, PCDFs, and PAHs have not been evaluated for this sampling train. However, the train design was based on a validated particulate emissions collection system (EPA Method 5) with the addition of an adsorbent cartridge (packed with XAD-2 resin) to collect vaporous emissions of semivolatile organics. The collection efficiencies of XAD-2 have been evaluated for a large number of compounds including PCBs and PAHs, and XAD-2 was selected for use in the EPA source assessment sampling system (SASS) train.[2,3] XAD-2 was also evaluated for use in a train specially designed for PCB sampling.[4]

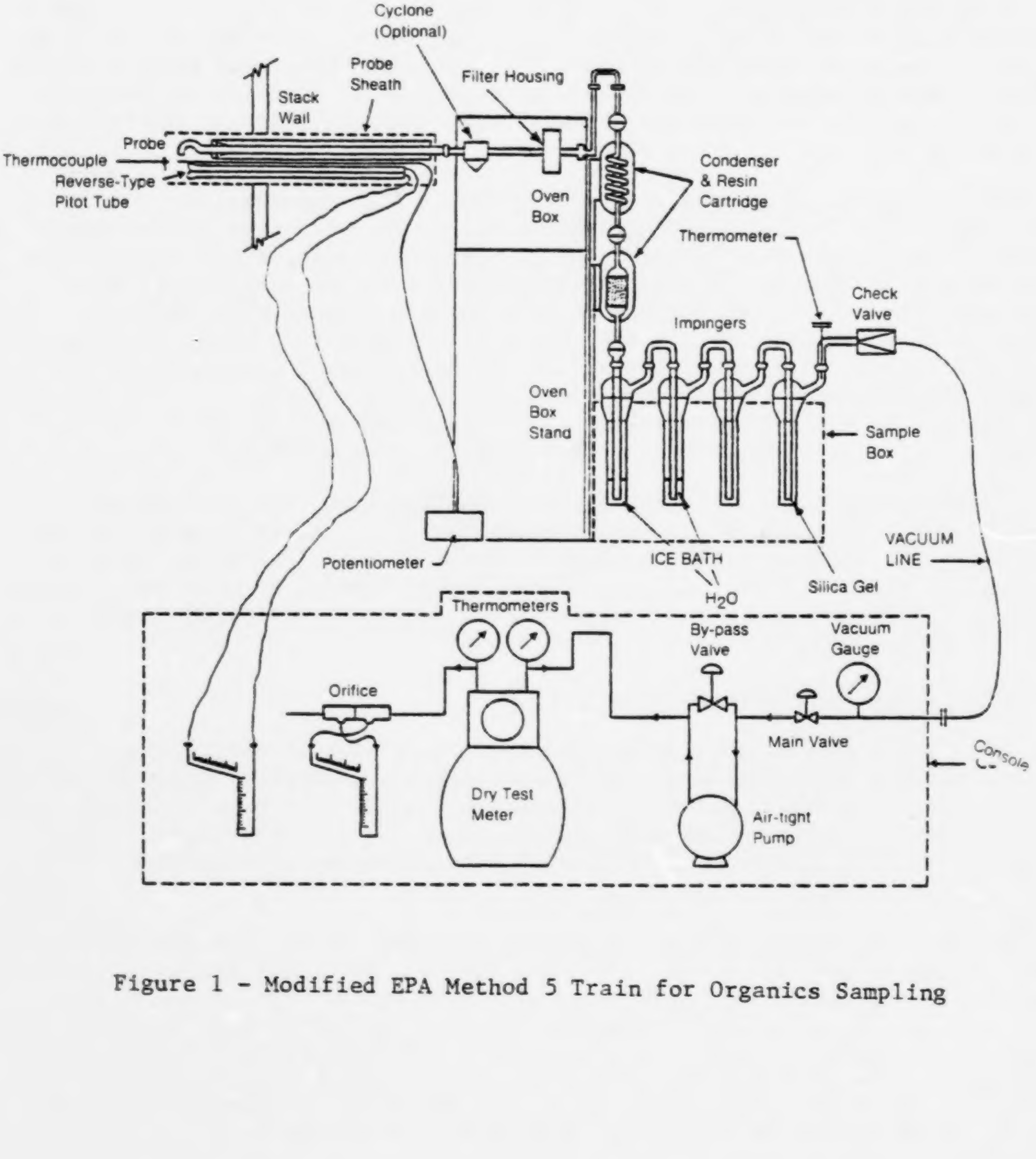
Cyclone (Optional)
Probe Sheath
Stack Wall
Filter Housing
Probe
Thermocouple
Reverse-Type Pitot Tube
Oven Box
Condenser & Resin Cartridge
Thermometer
Check Valve
Impingers
Oven Box Stand
Sample Box
Potentiometer
ICE BATH
H2O
Silica Gel
VACUUM LINE
Thermometers
By-pass Valve
Vacuum Gauge
Orifice
Main Valve
Console
Dry Test Meter
Air-tight Pump

Figure 1 - Modified EPA Method 5 Train for Organics Sampling

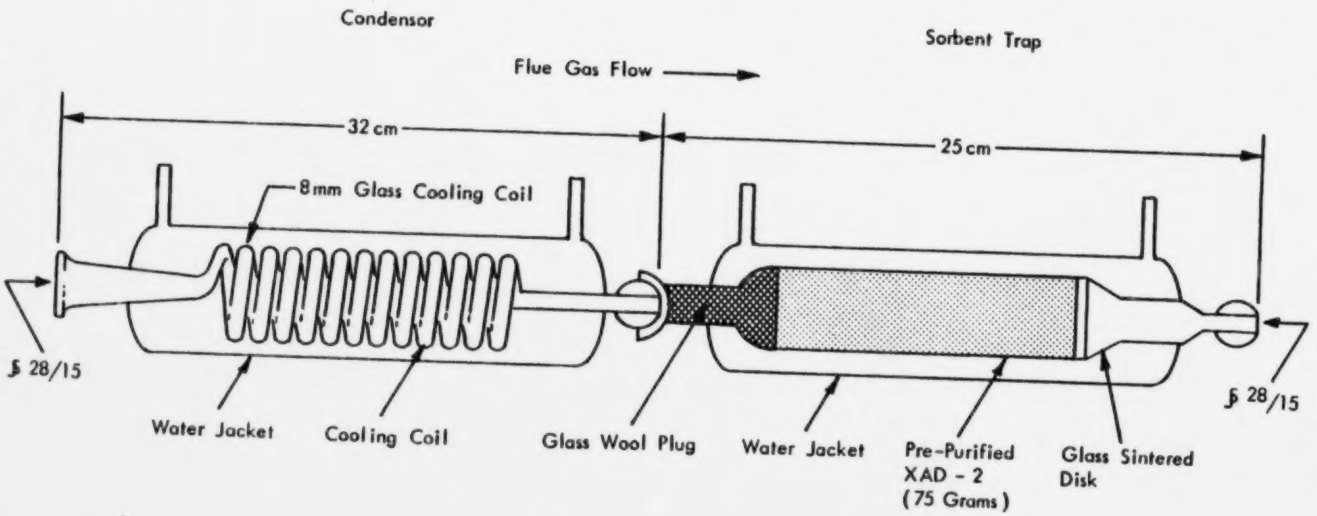
Condensor
Flue Gas Flow
Sorbent Trap
32 cm
25 cm
8mm Glass Cooling Coil
§ 28/15
§ 28/15
Water Jacket
Cooling Coil
Glass Wool Plug
Water Jacket
Pre-Purified XAD - 2 (75 Grams)
Glass Sintered Disk

Figure 2. Condensate and sorbent trap modification of the Method 5 sampling train for collection of organic vapors from flue gases.

Silicone Grease involves several steps. Removal of excess grease is accomplished by wiping clean with a rag. The joint is then dipped in warm concentrated KOH for 10 min, rinsed with distilled water, and wiped dry. The last traces of sealant are removed by dipping in chromic acid, followed by rinsing with distilled water and drying. Subsequently, the entire component should be washed in soap (such as Alconox®) and water, followed by at least three liberal rinsings of tap water and then distilled water. All apparatus are then rinsed with acetone (reagent grade) until all traces of water are removed. Finally, the glassware is rinsed sequentially with acetone and cyclohexane (Burdick and Jackson Distilled-in-Glass or equivalent), taking care to contact all sampling surfaces with the solvent. The components should be allowed to dry in a dust-free and organic-free area to minimize contamination of cleaned surfaces. The dried glassware should be protected by covering all open joints and exposed sample-contacting surfaces with solvent-rinsed aluminum foil and by subsequent storage in a closed airtight shipping container until use.

The filter housing gaskets should be cleaned using the same basic procedure with the following modifications. Do not allow non-TFE gaskets to soak in the 15% HNO_3 solution. Following the air drying, place the gaskets in a 225°F oven for 30 min to remove any moisture/solvents. Remove gaskets from the oven and, store in a clean, covered container.

It is highly recommended that TFE filter housing gaskets be used whenever possible as contact with silicon and rubber gaskets can cause significant sample contamination. If non-TFE gaskets must be used, care must be taken to avoid contact with the organic solvents, during sample recovery.

Sample storage containers must also be cleaned prior to use. All sample containers must be amber glass (or wrapped with aluminum foil) with TFE-lined caps. All bottles and sample recovery apparatus must be cleaned with soap and water, water rinsings, acetone rinsing and cyclohexane rinsing as outlined above.

Sorbent resin used in the sampling trains should be precleaned and its cleanliness verified prior to use. The recommended protocol for XAD-2 resins is outlined in the EPA Level 1 Procedures Manual.[3]

All aspects of sampling train assembly should be conducted under the cleanest laboratory conditions possible. To accomplish this, a limited-access field laboratory should be maintained at the site to minimize the possibility of airborne dust problems. Similarly, activities not directly related to train preparation or sample recovery should be done elsewhere. Finally, smoking should not be permitted in the laboratory.

Prior to assembly, all sample-contacting train surfaces should be rinsed with cyclohexane (Burdick and Jackson, Distilled-in-Glass or equivalent). Care must be taken to contact all surfaces with solvent. During assembly it is of vital importance that sealants, such as silicone grease, are not applied to any connecting joints. All train parts must be closely examined for any visual signs of contamination or defects that might induce sample error or downtime problems; corrections will be made if necessary. Leak sealing should be accomplished using a material that has a high boiling point and high thermal stability, such as the gas chromatography phase, Dow Corning DC 200. Sorbent cartridges must be protected from exposure to light during sampling, sample recovery, and shipping by wrapping each cartridge with aluminum foil.

Pretest Checkout of Sampling Apparatus

Briefly, the checkout involves assembling the entire sampling train as shown in Figure 1 without the probe. The fitting at the inlet of the filter box is sealed and the oven brought to operating temperature. The pump is turned on, and the flow meter gauges are observed for the existence of any appreciable flow. The train must pass the Method 5 standard leak test of less than 0.02 cfm at 15 in. of mercury or 4% of the sampling rate, whichever is less. If an unacceptable leak rate is observed, the operator should (starting at the pump and moving in the direction of the probe) tighten each fitting in order to assure that a loose fitting is not responsible for the leak. If this action does not solve the leak, the system should be leak checked on a modular basis until the problem is pinpointed. Under no condition should a sampling test be conducted with a leak rate in excess of 0.02 cfm at 15 in. Hg.

Flue Gas Sampling Procedures

Standard U.S. EPA methodology for particulate sampling, Method 5, as specified in the Federal Register[1] will be followed.

Two modified Method 5 sampling trains operating simultaneously should be used to traverse points at the center of equal areas within the stack. The number of traverse points and duration of sampling at each point should be provided to the sampling crews. The sampling rates should be adjusted to obtain samples at isokinetic conditions. The sum of flue gas collected each day in the two trains should total 20 m^3 ± 10%.

After the sampling trains are properly assembled and an acceptable pretest leak checkout has been made, preheat the probe and oven to 250°F. The stack temperature, moisture content, and velocity profiles must be determined. Compute the appropriate sampler flow rate and the proper nozzle size using the procedures and calibration curves supplied by the equipment manufacturer.

During the course of the sampling run, scheduled parameter checks should be made on flow rates, temperatures, and pressures. These data should be logged in a sampling record book. Sufficient ice must be kept in the impinger box to chill the condensor and resin trap to keep the impingers cool. At the conclusion of the sampling run, a post leak rate check should be performed.

Sample Recovery

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. During all rinsing, the approximate volumes of glass-distilled water, acetone, and cyclohexane used should be recorded. This is necessary for the determination of background contributions from the solvents. All organic solvents should be Burdick and Jackson

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Distilled-in-Glass or equivalent quality. The wash bottles used for all rinsings should be clean glass or TFE. Other plastic materials are unacceptable due to their potential for sample contamination.

When the probe can be safely handled, wipe off all external particulate matter near the tips of the probe nozzle. Remove the probe from the train and cap off the mating joints of both the probe and the train with solvent-rinsed aluminum foil. Also, cap the outlet of the train assembly after disconnection from the pump. Transfer the probe and train assemblies to the field laboratory for cleanup. This area should be clean and protected to minimize the chance of sample contamination or loss. Inspect the train prior to and during disassembly and note any abnormal conditions. Remove the sorbent trap from the train and cap it off. The cartridge should be transferred to the analytical laboratory intact for further sample recovery.

Rinse the probe with three portions each of water, acetone, and cyclohexane. Brush the entire length of the probe with a natural bristle brush during each rinse. The connecting tube between the sorbent module and the filter housing should then be subjected to sequential rinsings using acetone and cyclohexane, respectively. These rinses should be combined with the probe and filter holder rinses.

The filter particulate is recovered by carefully removing the used filter from the filter housing. Care must be taken to avoid tearing the filter or losing particulate sample. The filter should be stored in a suitable sealed glass container, such that the filter and its contents may be readily removed for weighing in the lab. After removal of the filter, both halves of the filter housing should be subjected to sequential rinsing with acetone and cyclohexane. These rinses should be combined with the preceding rinses. Non-TFE filter housing gaskets should not be rinsed during sample recovery.

When cyclones are employed, the cyclone particulate catch should be recovered and stored in a separate sealed glass container. The cyclone should be rinsed with water, acetone, and then cyclohexane. The rinses should be combined with the other rinses. Similarly, all remaining interconnecting tubing should be rinsed with acetone and cyclohexane. These rinses should be combined with previous rinses.

The contents of the first impinger (aqueous condensate) should be poured into a tared sample bottle. The bottle should be reweighed to ± 1 g and the weight recorded in the sampling record book. The impinger jar should be rinsed with acetone and cyclohexane and the rinses added to the sample bottle. Water accumulated in the remaining impingers should also be determined gravimetrically to ± 1 g.

Upon completion of the train recovery, at least four and possibly five samples should be recovered: (a) the resin cartridge, (b) filter particulate, (c) the first impinger contents, and (d) combined water, acetone, and cyclohexane rinses of the entire train forward of the sorbent trap. A cyclone catch will be the fifth sample if cyclones are employed.

The importance of thorough rinsing cannot be overstressed. Care must be taken to completely contact the interior surfaces of the train with each rinse to quantitatively remove the analyte material. Approximate rinsing volumes of each solvent used for each component should be recorded to allow the accurate determination of solvent background contributions. After all rinsing is completed, the sample bottle should be sealed and the volume of the contents marked to identify possible losses during shipment. All samples should be labeled and logged in the sampling record book as they are recovered. All samples and rinses should be refrigerated at 4°C (or stored in an ice chest) and exposure to light should be minimized during storage and shipment.

SOLID AND LIQUID SAMPLING

All sampling site locations should be clearly and appropriately labeled for easy identification. Also posted at the sample site should be an explanation of any subsample grid scheme to be followed. This serves as a reminder of specific details in subsampling. The crew chief should tour the sampling locations with the sampling personnel prior to the test to verify the collection procedure.

Crew chiefs should provide copies of all sampling schedules for the plant supevisor to post with the plant operations staff. This should provide for any necessary plant staff supervision or assistance in obtaining samples, or in the event of an emergency.

The solid and liquid sampling schedule will start at 0000 hr on the first day of flue gas sampling. Visits should to be made to sample sites as scheduled, and samples taken and placed into prelabeled bottles. Sample and container size required for typical media which should be sampled are given in Table 1. Also included are the recommended number of samples to be collected each day. All samples should be labeled and logged in the sampling record book as they are collected.

Stainless steel trowels, cups, and tongs and glass bottles should be used as necessary in sample capture. Long-handled extensions may be needed to reach some specific areas. Sampling tools should be kept free from contaminants and cleaned with methodology described in this manual. Collection of some samples may require special safety measures such as lab coat, work suit, plant staff or assistance. Safety should be a primary consideration in all sampling operations.

Solid and liquid sampling should continue through all three shifts each day. Sampling staff will have to determine a suitable schedule so all shifts are covered.

COMBUSTION AIR SAMPLING

Combustion air samples should be collected on 75 g of prepurified XAD-2 resin using vacuum pumps equipped with dry gas meters. A sampling rate of 0.75 cfm should be sustained until a total of 10-20 m^3 has been sampled. The resin should be placed in a cartridge similar to that in the sampling train, but without the condensor. The resin cartridge should be wrapped in aluminum foil to prevent photodegradation of the adsorbed organic compounds. The sorbent cartridge should be capped immediately after sampling has been completed to prevent contamination. This sample should be labeled and stored on ice as soon as possible after collection.

CONTINUOUS MONITORING

Continuous monitoring of the flue gas should be conducted during the period of flue gas sampling to aid in characterizing the efficiency of the combustion process and to provide an indicator of dramatic changes in the unit performance. The parameters monitored should include oxygen, carbon monoxide, carbon dioxide, and total hydrocarbons. The continuous monitoring probe should be inserted into the gas stream inlet to the air pollution control device to mitigate the influence of dilution by ambient air infiltration.

PROCESS DATA COLLECTION

In order to fully characterize the operation of the particular combustion facility it is necessary to collect the engineering data during flue gas sampling. A member of the sampling crew should be assigned to obtain pertinent information concerning the general description and design data and parameters for the power plant and air pollution control equipment that is not sufficiently described from the presite visit. In addition, details and schedules for soot blowing and ash removal during the actual testing period should be recorded. A member of the sampling crew should document any plant breakdown, maintenance, or operating problem during each day's test period that may have an impact on that day's test results. Process engineering data should also be recorded for the megawatt output, steam flow rate, coal loading (rate or total during each test period), and the operation of the electrostatic precipitators during each test period. The electrostatic precipitators should be monitored for operating voltages and amperages, rapping frequency, spark rate, and the number of inoperable units, if any. Information should also be obtained concerning the electrostatic precipitator installed on the unit. Specific parameters include the design volume, temperature, inlet concentration, number of precipitators, field array, gas passages per field, collecting surfaces, collecting surface spacing, face area per precipitator (ft^2), total surface (ft^2), gas velocity, and retention.

QUALITY ASSURANCE PROCEDURES

Calibrations

All sampling equipment should be calibrated prior to testing according to the procedures outlined for Method 5 sampling trains.[1] This should include probe nozzle diameter measurements, pitot tube, and dry gas meter calibrations as well as dial and liquid-filled thermometers and thermocouple-potentiometer system calibrations.

Field Blanks

The collection of field blanks is mandatory to indicate the cleanliness of all sample handling phases. A complete flue gas sampling train should be assembled in the field laboratory for use as a train blank at each plant. The probe and filter oven should be maintained at operating temperatures for a period equivalent to a typical sampling run. At the end of this period the train should be disassembled and the sample components recovered in the same manner as a flue gas sample.

Blanks of each rinsing solvent, as well as unused filters and resin cartridges, must be collected for blank determinations. The resin cartridges and filter blanks should be exposed to the same laboratory environment for the same time intervals as the sample filter and sorbent resin. Similarly, individual samples of acetone and cyclohexane rinse solvents must be collected from the wash bottles for each lot number solvent used. The volume of each solvent blank collected should be approximately equal to the solvent volumes used during the recovery of a sampling train. At least three unused sample bottles of each type should be designated as bottle blanks. All blank materials must be stored in clean sealed glass or TFE containers and treated as samples. Liquid volumes should be marked on the containers to monitor possible shipping losses.

SAMPLE CONTROL AND SHIPPING

An area designated for sample control and shipment preparation should be close to the field laboratory. This area should also have limited personnel traffic. Some stations may require lock and key access if outside of regular plant surveillance. The following shipment preparations should be done by staff on solid/liquid sampling duty.

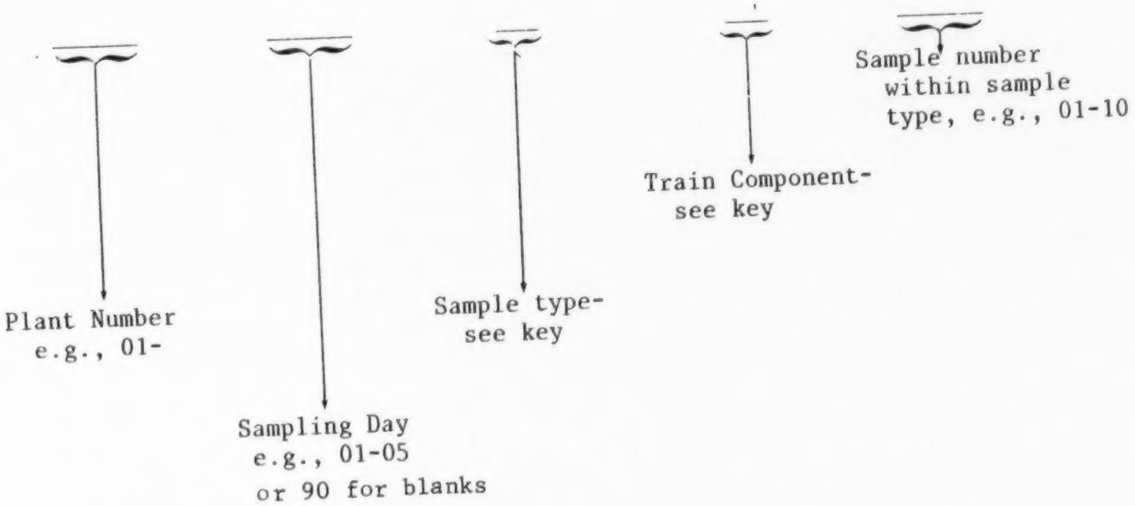
Properly labeled bottles should be supplied to the sample train recovery team. This team should then complete the label and return the full sample bottle and any necessary sampling or recovery remarks to the sample control and shipment operator.

Labels should be provided on computer printout paper and should be grouped by date. Each date should be subgrouped into air sample labels and solid and liquid sample labels. Extra labels should be provided at periodic intervals of the label packet.

All labels should be provided in duplicate. One label should be placed along the left column of a log book page each time a sample is labeled and secured in an ice chest. This will provide chronological entry of sample codes in the log book. Any sampling remarks should be recorded along side the label. Also to be included in this right margin is the sample cooler number in which the corresponding labeled sample has been placed.

MRI's labeling system provides an 8-digit number on each label to be used for primary sample tracking. The label number is defined in Figure 3. The label will also contain a 16-character sample code which provides for easy, accurate identification. This sample code is defined in Figure 4.

LABEL CODE


Sample number within sample type, e.g., 01-10
Train Component- see key
Sample type- see key
Plant Number e.g., 01-
Sampling Day e.g., 01-05 or 90 for blanks

SAMPLE TYPE

0 - Flue Gas Outlet
1 - Bottom Ash
2 - Control Device Ash (Fly Ash)
3 - Combustion Air
4 - Coal
5 - Refuse-Derived Fuel

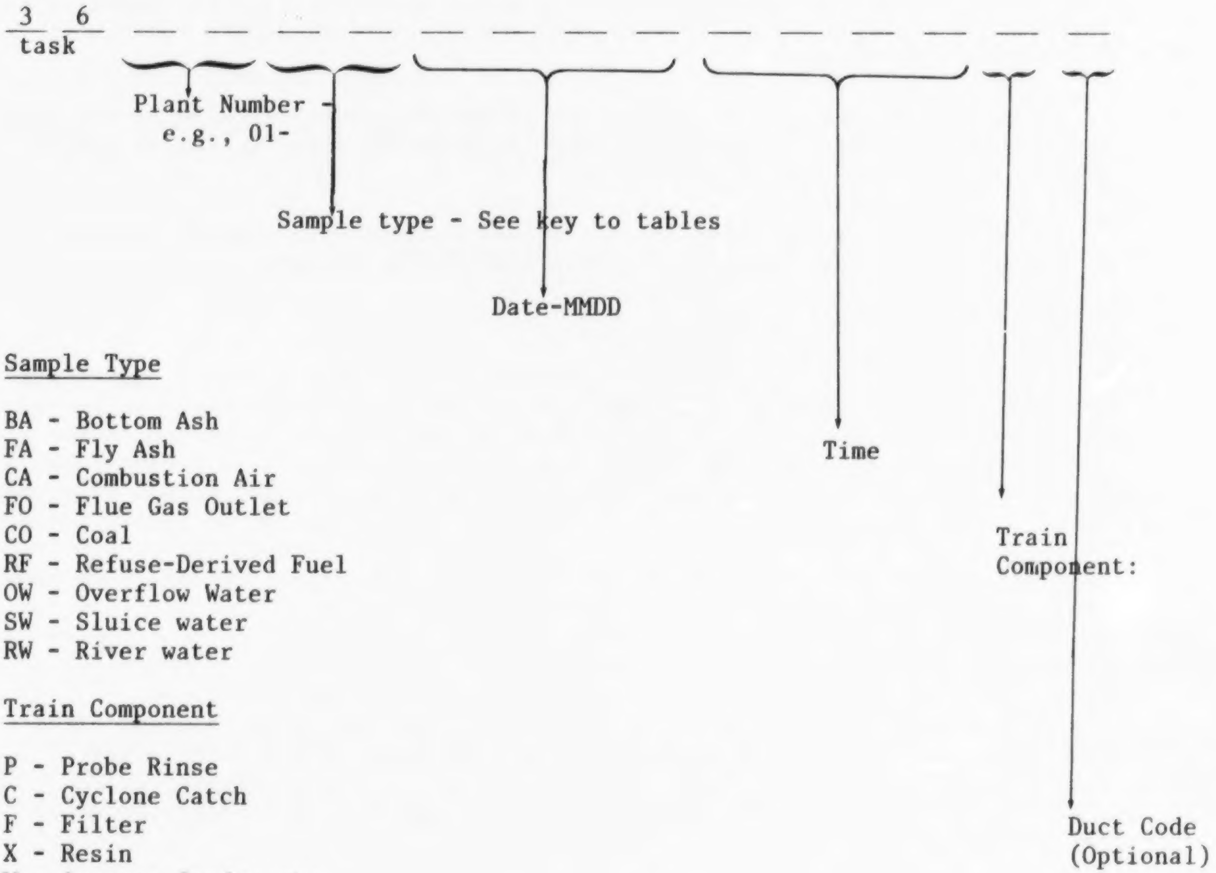
Water sources will be numbered and defined as they are taken.

TRAIN COMPONENT

0 - No Component
1 - Probe Rinse
2 - Cyclone Catch
3 - Filter
4 - Resin
5 - Aqueous Condensate

Figure 3. Eight-digit label code for stationary combustion source samples.

SAMPLE CODES


3 6
task
Plant Number -
e.g., 01-
Sample type - See key to tables
Date-MMDD
Time
Train
Component:
Duct Code
(Optional)

Sample Type

BA - Bottom Ash
FA - Fly Ash
CA - Combustion Air
FO - Flue Gas Outlet
CO - Coal
RF - Refuse-Derived Fuel
OW - Overflow Water
SW - Sluice water
RW - River water

Train Component

P - Probe Rinse
C - Cyclone Catch
F - Filter
X - Resin
W - Aqueous Condensate

Figure 4. Sixteen character sample code for stationary combustion source samples.

All labels should be prepared so that minimum amount of additional information must be entered in the field. The time of sample capture, any subsampling location designations, and the sampler's name are typically the only entries. All entries must be made on the duplicate label as well.

Labels should be self-adhesive. In addition, 1-1/2 to 2 in. transparent tape should be overlaid on the completed label placed on sample containers as a precautionary measure.

All liquid samples should have the volume marked on the side of the shipping container with a permanent marker. This should allow losses of sample from handling and shipping to be noted.

Samples other than those in amber glass bottles will require special packaging. These are given in the following two paragraphs.

Modified Method 5 Particulate

The particulate filters should be returned to their original containers (petri dishes) when sampling is completed. Each petri dish should be taped shut using masking tape. The identification label should be placed on the top center of each dish. The filter and dish number should be included on both labels. The dish should be wrapped in aluminum foil and sample ID number (from label) copied onto top side. The petri dish should be carefully sealed in a ziplock bag, with a minimum air space. Care must be taken to ensure that filters are returned to the original containers since it is necessary to know the predetermined weight of each specific filter.

Resin Cartridge

The sample identification label should be affixed to the aluminum foil covering. The entire cartridge should be wrapped in an adequate amount of bubble pack (bubbles to inside) with cartridge ends capped securely with glass balls. A lab marker should be used to copy the label ID number on to the outside of the wrap.

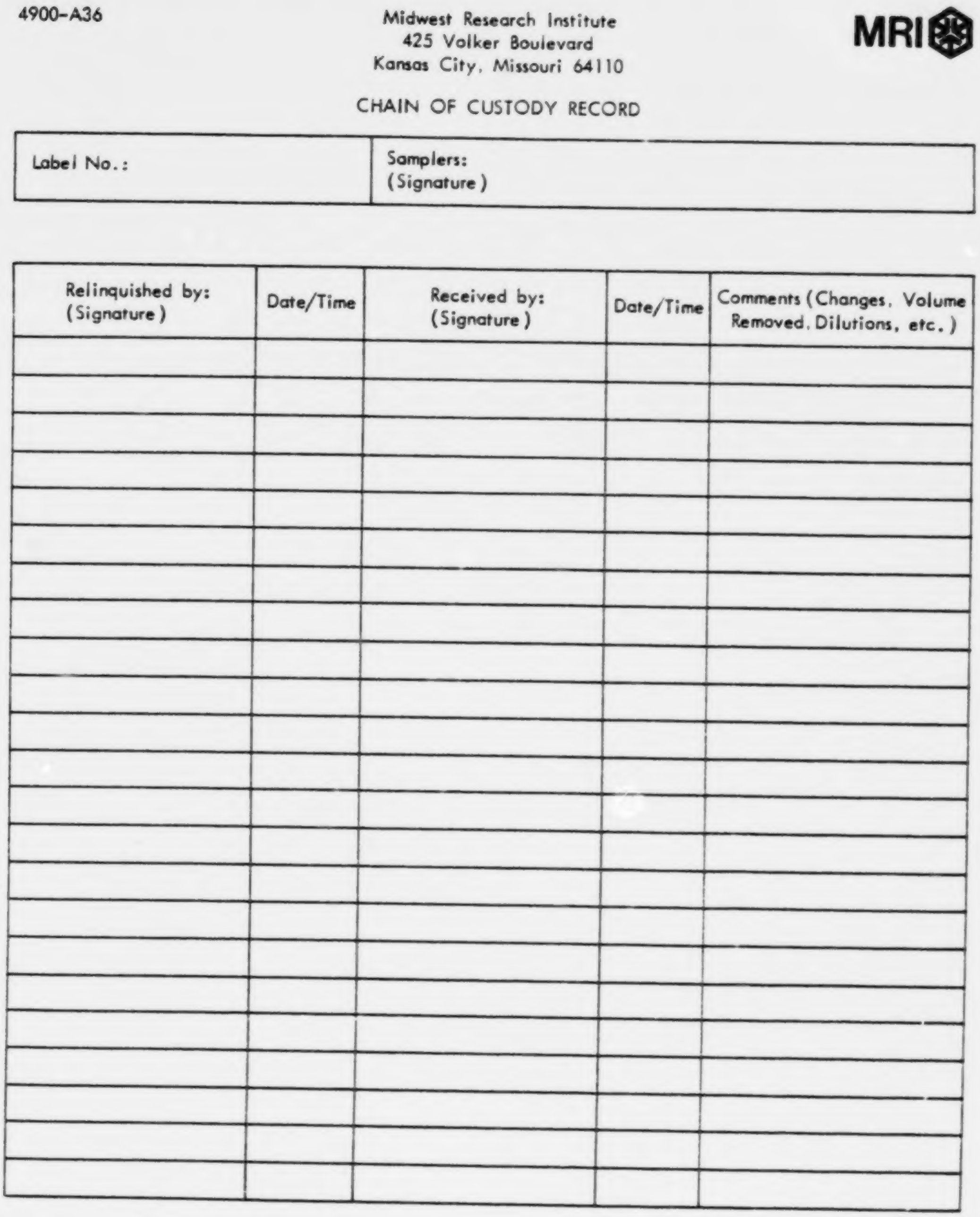
Sample Custody Documentation

A chain-of-custody record should be prepared for every sample. The custody sheet should be initiated in duplicate immediately after the sample has been labeled. It should include the sample label number and the sampler's signature. At the time of sample shipment, the record should be signed and the time and date should be noted. The original copy of the chain-of-custody record should be enclosed in the sample container. The yellow copy should be retained by the crew chief until the samples are received and logged in at the analytical laboratory.

When the container arrives at the laboratory, the person who will be preparing the samples should receive (take custody of) it. That person should then open the shipping container and check each sample for damage or tampering. This person should then sign all the enclosed chain-of-custody records and note any damage or indication of tampering.

Whenever custody of the sample is transferred from one person to another, the person relinquishing custody of the sample should sign the chain-of-custody form and note the time and date. The person receiving the sample should do the same. The person having custody of the sample should have sole control of access to the sample.

Figure 5 is an example of a chain-of-custody record used by MRI.



4900-A36

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

MRI

CHAIN OF CUSTODY RECORD

Label No.:	Samplers: (Signature)

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Date/Time	Comments (Changes, Volume Removed, Dilutions, etc.)

Figure 5. Sample custody transfer sheet used by MRI.

SECTION 3

SAMPLE ANALYSIS

The analytical procedures described in this section were developed during a pilot study of stationary combustion source facilities. The primary objective of this section is to ensure that the extraction and analysis of samples from other such facilities is coordinated and consistent for all laboratories involved in possible future Exposure Evaluation Division programs.

Each of the different types of samples should be combined into daily composites, extracted, and analyzed by capillary gas chromatography using flame ionization and Hall (halide mode) electrolytic conductivity detectors (HRGC/Hall-FID) and by capillary gas chromatography/mass spectrometry (HRGC/MS) using fused silica columns. The analytical scheme presented in Figure 6 should be followed to determine the presence of various compounds in sample extracts. Both qualitative and quantitative results are expected for the range of polycyclic and chlorinated organic compounds determined by these procedures. A rigorous quality assurance/quality control program has been outlined and should be considered by other laboratories participating in similar analytical efforts. In addition, a procedure to determine total organic chlorine (TOCl) is described. This technique may be beneficial for pilot studies to provide a more sensitive means of identifying the presence of chlorinated polycyclic compounds.

GENERAL ANALYTICAL PROCEDURES

All solvents should be Burdick and Jackson, Distilled-in Glass, pesticide grade quality, or equivalent. Glass wool, boiling chips and anhydrous sodium sulfate should be pre-extracted with a hexane-acetone mixture or benzene. The anhydrous sodium sulfate should be extracted with the hexane-acetone azeotropic mixture, air dried, heated at 110°C for several hours, and finally baked at 650°C for at least 2 hr. It is important to allow the extracted Na_2SO_4 to dry thoroughly before baking at high temperature to avoid explosions in the high temperature oven.

All glassware that will be used in handling the samples and extracts should be cleaned first with soap and hot water, rinsed thoroughly with hot water, followed by distilled water. Acetone (reagent grade) should be used to rinse glassware for removal of all traces of water and final rinses with acetone and cyclohexane should be required. If blanks are a problem, the glassware should be baked at 400°C for at least 8 hr prior to use.

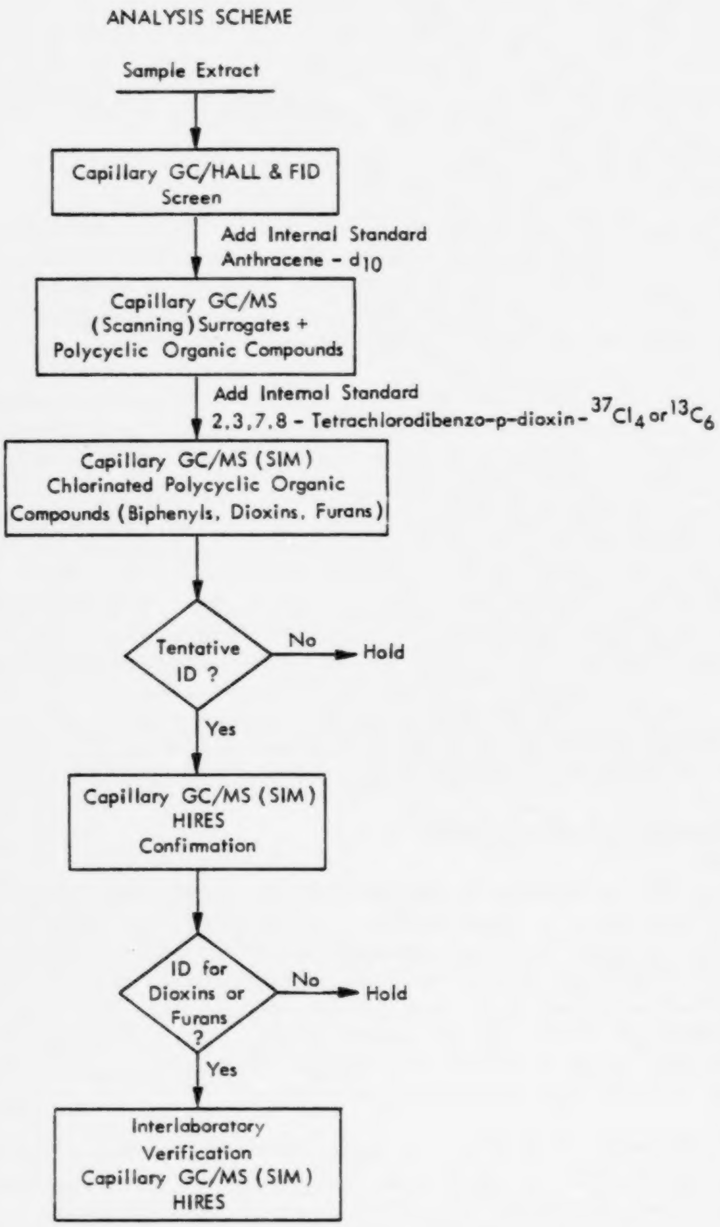

ANALYSIS SCHEME
Sample Extract
Capillary GC/HALL & FID Screen
Add Internal Standard Anthracene - d_{10}
Capillary GC/MS (Scanning) Surrogates + Polycyclic Organic Compounds
Add Internal Standard 2,3,7,8 - Tetrachlorodibenzo-p-dioxin-$^{37}Cl_4$ or $^{13}C_6$
Capillary GC/MS (SIM) Chlorinated Polycyclic Organic Compounds (Biphenyls, Dioxins, Furans)
Tentative ID ?
No
Hold
Yes
Capillary GC/MS (SIM) HIRES Confirmation
ID for Dioxins or Furans ?
No
Hold
Yes
Interlaboratory Verification Capillary GC/MS (SIM) HIRES

Figure 6. Analysis scheme for sample extracts.

EXTRACTION

The sample extraction methods described below have been developed to maximize recovery of a wide range of PAH compounds and polychlorinated aromatics. Each sample should be spiked with labeled surrogate compounds prior to extraction for component recovery determinations.

Solid Samples

All solid samples should be Soxhlet extracted for 8 to 24 hr using benzene (Burdick and Jackson, Distilled-in-Glass or equivalent) as the solvent. Solid samples include XAD-2 resin, filters from the filter catch, and the cyclone catch from the modified Method 5 train, control device ash (fly ash), bottom ash, and fuel.

Samples from the Modified Method 5 sampling train should be extracted simultaneously. For example, filters from the filter catch taken for a single day's operation may be combined and extracted in the same Soxhlet apparatus. However, sampling train materials should not be mixed (e.g., XAD-2 resin, filters, cyclone material) since XAD-2 resins may be reclaimed. The filters from the filter catch should be weighed prior to extraction. The weight of the collected particulate matter should be calculated from measurements for each filter made prior to sampling the field. No attempt should be made to achieve constant weights for the filter samples. Also, the particulate material obtained from the cyclone and probe rinses should be weighed prior to extraction.

Control device ash and bottom ash should be individually composited for each sampling day and 20 g each of these media Soxhlet extracted with benzene for 8 to 24 hr. Prior to extraction, 10 ml of organic-free water should be added to the control device ash. If the bottom ash is dry, 10 ml of water should also be added to wet the material before beginning the extraction. An inert material, such as Chromosorb W can be added to ash samples to promote more efficient solvent flow through the sample.

Coal (10 g) should be Soxhlet extracted with benzene (8 to 16 hr). Large mesh coal samples should first be ground to a powder using a ceramic mill with stainless steel balls. Refuse-derived fuel will be evaluated when homogeneous samples are available. This material (10 to 20 g) should also be milled and Soxhlet extracted with benzene as the solvent for periods of 8 to 24 hr. This extract should be washed three to four times with 100-ml aliquots of organic free water.

All extracts should be dried by passage through short columns of anhydrous sodium sulfate. The dry extracts should be concentrated in Kuderna-Danish appartus to approximately 5 ml. The extracts from the various components of each day's flue gas sample should be combined and reduced to 5 ml in a Kuderna-Danish evaporator. The extracts should be further concentrated to 1 ml with a gentle stream of purified nitrogen. If solids precipitate from extracts during concentration, slowly dilute and stir the extract to redissolve the solids. Do not attempt to further concentrate the extract.

Aqueous Samples

Aqueous samples may be obtained as plant influents and effluents, as well as from the combined train rinses from flue gas sampling and the aqueous condensate from the first impinger. The combined train rinses should include water, acetone, and cyclohexane. This sample should be shaken vigorously and the organic layer removed using a separatory funnel. Two 60-ml aliquots of cyclohexane should be used to extract the aqueous solution. The cyclohexane extracts should be combined, dried by passing through a short column of anhydrous sodium sulfate, and finally combined and reduced with other extracts from the modified Method 5 sampling train. If emulsions are formed during the extraction, 2 to 3 g of sodium sulfate can be added to the mixture to promote adequate separation. The extracts should be dried and concentrated in the same manner as extracts from solids.

EXTRACT FRACTIONATION/CLEANUP

Sample extracts, particularly the flue gas samples, may contain considerable interferences that may present problems in the effective analysis of such compounds as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans or the surrogate compounds. These extracts should be cleaned by EPA Method 613 to simplify the sample matrix prior to analysis for polychlorinated dibenzo-p-dioxins and dibenzofurans. Since other polycyclic organic compounds may be lost by this cleanup procedure, and it may be necessary to fractionate a portion of sample by other techniques, such as silica or florisil adsorption chromatography, prior to GC/MS analysis. Only half of a sample extract should be submitted to any fractionation scheme. It is also important to measure the exact volume of a sample extract subjected to cleanup to ensure valid quantitation of specific compounds on the final aliquot.

EXTRACT ANALYSIS

HRGC/Hall-FID

Each extract should be screened first for the presence of halogenated organic compounds by capillary gas chromatography separation with a Hall electrolytic conductivity detector operated in the halogen specific mode. Fused silica capillary columns, 30 m in length and coated with SE-54 [1% vinyl in poly(methylphenylsiloxane) previously deactivated by silylation], 0.25 mm ID, will be used for gas chromatography separations of all extracts.

On-column and direct injection techniques are preferred, but Grob-type splitless injectors may be used, if necessary. The extracts should be chromatographed using the following temperature program: isothermal at 60°C for 2 min, increase temperature at 10°/min to 300°C and hold isothermally for 15 min. The qualitative results from these analysis should be useful in identifying the presence of halogenated compounds by gas chromatography/mass spectrometry analyses. Large halogen responses at specific retention times should identify the regions of the chromatograms where interpretation of the mass spectra data may lead to the identification of halogenated compounds.

HRGC/MS (Scanning)

The correlation of the mass spectral data with halogen responses from the Hall electrolytic conductivity detector is necessary for positive identification of chlorinated organic compounds in the sample extract. Therefore, it is necessary to duplicate gas chromatography conditions for the two methods. Fused silica capillary columns coated with SE-54, 15 to 30 m in length, should be used for all scanning HRGC/MS studies. On column, direct, or Grob-type splitless injections should be used and the same temperature program used for HRGC/Hall-FID should be followed.

Mass spectra should be acquired over the range of m/e 40 to 500 at a rate of 1 to 1.2 sec/scan. The spectral data from these analyses should be used for both qualitative and quantitative determinations. The compounds that are positively identified and are of sufficient concentration should be quantitated by peak area from the total ion chromatogram versus the peak area of the appropriate internal standard.

HRGC/MS Selected Ion Monitoring (HRGC/MS-SIM)

The selected ion monitoring (SIM) technique should be used to determine the presence of chlorinated dibenzodioxins or dibenzofurans. Preliminary indications of the presence of these compounds may be evident from results of the HRGC/Hall-FID and HRGC/MS (scanning) experiments. However, the HRGC/MS-SIM technique has greater sensitivity for determination of these compounds in the sample extracts. Selected ions characteristic of the mono- through octachloro PCDDs, PCDFs, and PCBs should be monitored by this technique. The criteria for the identification of these analytes in any extract will be dependent on the coincidence of peaks in the extracted ion current plots of the characteristic ions at the appropriate retention times and on the characteristic relative intensity ratios of these selected ions. Table 2 lists the HRGC/MS-SIM ions that should be used to identify the presence of the dibenzodioxins, dibenzofurans, and biphenyls. Fused silica capillary columns coated with Carbowax 20M or other polar materials may be used for isomer specific SIM analyses for polychlorinated dibenzodioxins and dibenzofurans.

HRGC/MS High Resolution Mass Spectrometry (HRGC/HRMS)

The tentative identification of dibenzodioxins and dibenzofurans by HRGC/MS-SIM in any extract should be confirmed by HRGC/HRMS. This procedure should be used to verify the presence of these compounds in any sample extract. Positive identifications of chlorinated dibenzodioxins or chlorinated dibenzofurans by HRGC/HRMS should be supplemented by verification by other accredited laboratories with HRGC/HRMS capabilities. All HRGC/HRMS studies should employ fused silica capillary columns coated with either SE-54, Carbowax 20M, or other materials capable of providing equivalent or better chromatographic resolution.

TABLE 2. GC/MS-SIM IONS

Number of chlorines	Biphenyls	Dibenzofurans	Dibenzo-p-dioxins
1	188/190	202/204	218/220
2	222/224	242/244	252/254
3	256/258	270/272	286/288
4	290/292	304/306	320/322
5	324/326	338/340	354/356
6	360/362	374/376	390/392
7	394/396	408/410	424/426
8	428/430	442/444	458/460
9	462/464	-	-
10	498/500	-	-

Total Organic Chlorine (TOCl) Measurements

TOCl measurements may be used in a primary sensitive screen of the chromatographable organically bound halide contents of extracts prepared for GC/MS analysis in tiered analytical schemes. The TOCl procedure is a simplified gas chromatographic method using a Hall electrolytic conductivity detector in the halide mode. A short packed GC column (typically 1-2 in. x 1/4 in. ID) and a rapid temperature program are used to elute all chromatographable compounds with volatiles equal to or greater than dichlorobenzenes as a single peak. The area of this peak constitutes the TOCl response which is quantitated as chloride against a mixture of chlorinated compounds (typically a PCB mixture such as Aroclor 1254). The typical method senstivity is 0.25-2 ng chloride.

QUALITY ASSURANCE (QA) PROCEDURES

The positive identification and quantitation of specific compounds in this assessment of stationary conventional combustion sources is highly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section were designed to monitor the performance of the analytical methods and to provide information to take corrective actions if problems are observed. These procedures are summarized in Table 3.

Field Blanks

The field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and are expected to be handled with exactly the same procedure as each sample medium.

Method Blanks

A method blank should be prepared for each set of analytical operations. This will evaluate contaminations and artifacts that are derived from glassware, reagents and sample handling in the laboratory. Method blanks should be evaluated by each laboratory for solid and aqueous sample extractions.

Recovery Spikes

Surrogate compounds should be added to all samples prior to extraction to provide an accurate record of analyte recovery. Specific analytes should be used for method development procedures. In either case, duplicate samples should be prepared. The surrogate compounds should include napthalene-d_8 and chrysene-d_{12}. The other compounds that will be used as surrogates include pentachlorophenol-$^{13}C_6$, 1,2,4,5-tetrachlorobenzene-$^{13}C_6$, and 3,4,3',4'-tetrachlorobiphenyl-d_6.

Internal Standards

Each concentrated extract should be spiked with anthracene-d_{10} prior to analysis by HRGC/MS in the scanning mode. This should allow for adequate quantitation of specific analytes in the extracts once proper response ratios have been established using standard solutions. This internal standard should be added to the extracts to yield a concentration in the range of the analytes and the surrogate compounds. This internal standard can also be used to determine relative retention times in any particular chromatograms, and this provides another means of analyte identification. Stable isotope labeled isomers of tetrachlorodibenzo-p-dioxin and tetrachlorodibenzofuran should be used for selected ion monitoring methods for these specific compounds. The isotope label should provide sufficient distinction of the internal standard and the actual isomers present in the sample extracts.

Reference Materials

A reference ash will be prepared by compositing ash from several facilities by MRI. Portions of this ash may be sent to interested laboratories as a means of evaluating interlaboratory performance. Two samples of spiked reference ash and two samples of unspiked reference ash will be submitted to all laboratories. These samples will be extracted and analyzed with the same procedure used for all other samples.

Capillary Column Performance Tests

The optimum performance of the fused silica capillary columns coated with SE-54 is an integral function of the separation and identification of specific compounds in the sample extracts. Therefore, each laboratory should frequently evaluate the performance of capillary columns used for extract analysis. Grob-type test mixtures should be used to evaluate each column used for GC/Hall and GC/MS studies. A test mixture prepared with halogenated compounds should be used to test capillary columns with Hall electrolytic conductivity detectors.

TABLE 3. SAMPLING AND ANALYSIS QUALITY ASSURANCE

Field blanks

Method blanks

Recovery spikes - analytes
surrogates
d_8-napthalene
d_{12}-chrysene
$^{13}C_6$-1,2,4,5-tetrachlorobenzene
d_6-3,4,3',4'-tetrachlorobiphenyl
$^{13}C_6$-pentachlorophenol

Internal standards - d_{10}-anthracene
^{37}Cl-TCDD or ^{13}C
^{37}Cl-TCDF

Reference materials

Capillary column performance checks

Interlaboratory verification

The parameters that should be monitored include separation number (Tz) for a homologous series of compounds, the height equivalent for theoretical plates (HETP), the number of theoretical plates (N), peak asymmetry, adsorption ratios, and pH of the column. Peak asymmetry is calculated for each peak of the test mixture from the formula:

$$AS = \frac{W_b}{W_f} \times 100$$

Where W_b and W_f are the back and front baseline widths of the peak measured from a line bisecting the peak maximum. Adsorption ratios are determined by comparison of the peak height for a compound susceptible to adsorption with that of an inert compound. The pH of a column can be determined from the ratio of the peak heights of equivalent quantities of an acid and a base in the test mixtures.

The capillary columns should be evaluated immediately upon installation and at least once per week. The capillary columns should be rejected for poor performance as related to separation number, adsorptivity, and pH. The columns should be tested more frequently if drastic deterioration of the column is noted in a 1-week time span.

Interlaboratory Verification

All extracts in which polychlorinated dibenzodioxins and dibenzofurans are identified by HRGC/MS or HRGC/HRMS should be submitted to other laboratories for confirmation of these identifications by HRGC/HRMS.

SECTION 4

DATA REPORTING

The following section provides examples of the pertinent data that should be reported for characterization of polycyclic organic matter from stationary combustion sources. Examples are given for methods of sample tracking through the entire organic compound analyses, reporting of analytical data for surrogate compounds and the inputs and emissions of particular analytes, and the reporting of the engineering process data necessary for describing flue gas sampling methods and the actual combustion process. It is highly recommended that all laboratories involved in combustion facility characterizations for polycyclic organic materials adhere as closely to these reporting guidelines to facilitate comparision of data from several sources.

SAMPLE TRACKING (ANALYTICAL)

Sample tracking sheets should be used by all analytical laboratories to monitor the status of sample analyses. An example of the tracking sheet is shown in Table 4. The sample numbers illustrated are truncated when samples for 1 day's operation are composited. The pertinent information presented in this sample number includes the task number (36), plant number, and the date sampled.

The sample tracking sheets should be initiated upon receipt of the samples from the field stations. The information on the sheets should include dates samples were received and dates the samples were composited and extracted. The other designations should indicate the extent of analysis for each composited sample, i.e., screening sample by HRGC/Hall-FID, HRGC/MS, and HRGC/MS-SIM. Other remarks can be added as required. For example, PAH, PCDD, or PCDF might be added to indicate that polynuclear aromatic hydrocarbons, chlorinated dibenzodioxins, or chlorinated dibenzofurans have been tentatively identified in particular extracts. Likewise, other abbreviations might be added for identification of chlorinated benzenes or phenols. Target may be used to indicate that analysis for specific compounds has been completed. Major will be used to specify that the major components of a sample have been investigated.

DATA MANAGEMENT AND REPORTING

The data generated for the target compounds and the major components of each sample extract should be presented to MRI in two forms. Assessment of the QA program should be accomplished by reporting percent recovery of the surrogate compounds in a specific extract together with the concentrations of the target and major compounds in the extracts. Concentrations for the target

TABLE 4. SAMPLE TRACKING SHEET

Sample no.	Received	Compos-sited	Ex-tracted	HRGC/ Hall-FID	HRGC/MS (Scanning)	HRGC/ MS-SIM	To MRI HRGC/ HRMS
36/03/FA/0330	0415	0418	0418	4-20	4-23 Target	4-27 Target	4-29
36/03/BA/0330	0415	0418	0418	4-20	4-23 Major Target	4-27	
36/03/CA/0330	0415	0418	0418	4-20	4-25	4-27	
36/03/FO/0330	0415	0419	0419	4-21	4-25		
36/03/CW/0330	0415	0419	0419	4-21	4-25		

compounds should be reported for all extracts. If a compound is present but cannot be quantitated, it should be reported as less than the detection limit. If a compound is not detected, it should be reported as not detected. The data for QA will be reported as shown in Table 5. The percent recovery should be reported for the surrogate compounds only.

TABLE 5. ANALYTICAL DATA REPORTING SHEET

Day 1 Bottom ash - Composite ID No.

Surrogate compounds	Concentration	% Recovery
d_8-Naphthalene		
c_{12}-Chrysene		
$^{13}C_6$-1,2,4,5-Tetrachlorobenzene		
$^{13}C_6$-3,4,3',4'-Tetrachlorobiphenyl		
$^{13}C_6$-Pentachlorophenol		
Analyte Compounds		
1.		
2.		
3.		
4.		

The other method for reporting the data should follow the concentration of a particular compound in all sample matrices. Sample concentrations should be grouped according to inputs and outputs of the plant. This data report should be presented as shown in Table 6, representative for particular compounds over five composited sampling days.

The data supplied by the engineering report will be used to determine the mass flow inputs and emissions for the various sample media. The summary of the flue gas sampling and the continuous monitoring data should be tabulated as shown in Table 7.

TABLE 6. TOTAL INPUTS AND EMISSIONS

	Inputs						Emissions					
	Combustion			Coal			Flue gas			Bottom ash		
Composite day	Mass input (dscm/hr)	Conc. (ng/g)	CA input (mg/hr)	Feed rate (kg/hr)	Conc. (ng/g)	Coal input	Mass emissions (dscm/hr)	Conc. (ng/dscm)	FO emissions (mg/hr)	Mass flow (kg/hr)	Conc. (ng/g)	BA emissions (mg/hr)
I												
II												
III												
IV												
V												
Mean $\bar{x}$												
Standard deviation												

	Emissions							
	Fly ash			Miscellaneous outputs (water)				
Composite day	Mass flow (kg/hr)	Conc. (ng/g)	FA emissions (mg/hr)	Mass flow (ℓ/hr)	Conc. (ng/ℓ)	WO emissions (mg/hr)	Total inputs (mg/hr)	Total outputs (mg/hr)
I								
II								
III								
IV								
V								
Mean $\bar{x}$								
Standard deviation								

TABLE 7. DAILY FLUE GAS SAMPLING DATA

Date (1980)	Test no.	Train no.	Sample Volume		Gas composition[a]				Stack temperature °F	Molecular weight	Moisture %	Velocity ft/sec	Gas flow			Isokinetic rate %
			DSCF	DSCM	O_2 %	CO_2 %	CO ppm	THC ppm					ACFM	DSCFM	DSCMM	
	1															
	2															
	3															
	4															
	5															

[a] Average during test period.

SECTION 5

REFERENCES

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3. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA 600/7-78-201 (October 1978).

4. Haile, C. L., and E. Baladi, "Methods for Determining the Total Polychlorinated Biphenyl Emissions from Incinerator and Capicator- and Transformer-Filling Plants," NTIS No. PB-276 745/761 (1977).

Sample C. Technical Report Data Sheet, EPA Form 2220-1

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
560/5-82-014

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
Sampling and Analysis Procedures for Assessing Organic Emissions from Stationary Combustion Sources for EED Studies. Methods Manual

5. REPORT DATE
12/1/81 Preparation Date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-01-5915

12. SPONSORING AGENCY NAME AND ADDRESS
Exposure Evaluation Division (TS-798)
Office of Pesticides and Toxic Substances
401 M Street, SW
Washington, DC 20460

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The sampling and analysis methods described in this report were specifically designed for use in an ongoing nationwide survey of emissions of organic pollutants from stationary combustion sources. The primary focus of this survey is on polynuclear aromatic hydrocarbons (PAHs) and polychlorinated aromatic hydrocarbons including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). To date, these procedures have been used by Midwest Research Institute (MRI) to survey emissions from coal-fired utility boilers, a co-fired (coal + refuse-derived fuel) utility boiler, and a municipal refuse incinerator. This document was prepared by MRI as a guideline for laboratories who may participate in this study, and for other researchers who wish to use these methods.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sampling and Analysis	PAH	
Methodology	PCDD	
Combustion	PCDF	
Emissions	POM	

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
34

22. PRICE

EPA Form 2220-1 (9-73)